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BIOFILTRATION DU MÉTHANE EN ABSENCE OU EN PRÉSENCE D'ÉTHANOL EN RÉGIME PERMANENT OU EN RÉGIME TRANSITOIRE

Methane biofiltration in the absence and presence of ethanol vapors under steady state and transient state conditions

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To my mother and my father

RÉSUMÉ

Les émissions de méthane (CH_4), gaz à effet de serre provoquant le réchauffement climatique doivent être contrôlées. Les biofiltres peuvent être utilisés pour atteindre cet objectif. Les émissions de CH_4 issues des industries agroalimentaires ou du traitement des eaux peuvent être accompagnées de vapeurs d'alcool. La présence simultanée de CH_4, polluant à limitation par transfert de masse et d'alcool, polluant à limitation cinétique dans un mélange gazeux peut induire des limitations dans le biofiltre. L'objectif principal de cette recherche est l'évaluation des limitations dans un biofiltre traitant le CH_4 en présence ou en absence de vapeur d'alcool en régime permanent ou transitoire. Dans un premier temps, une revue de littérature s'est penchée sur les limitations basées sur le transfert de masse et la cinétique lors de l'enlèvement de polluants organiques dans un biofiltre. Par la suite, l'élimination du CH_4 a été effectuée dans un biofiltre afin d'évaluer l'influence de la concentration à l'entrée du biofiltre sur la performance du biofiltre. Une capacité d'élimination maximale de 45 g m^{-3} h^{-1} a été obtenue pour une charge à l'entrée de 87 g m^{-3} h^{-1} du biofiltre. Le biofiltre a toléré des charges par à-coups de CH_4 de même que des privations de CH_4 et de nutriments. Par conséquent, les comportements en régimes permanent et transitoire d'élimination du CH_4 en présence de vapeurs d'éthanol ont été étudiés dans un biofiltre ayant un lit filtrant inorganique sous des temps de résidence en fût vide (EBRT) de 6, 3 et 1.5 minutes. L'ajout d'éthanol sur 3 cycles a été effectué en fonction des 3 EBRTs. Un EBRT de 6 min correspondant à des charges à l'entrée de CH_4 et d'éthanol de 4.5 et de 132 g m^{-3} h^{-1} a induit des limitations mineures en ce qui a trait à l'enlèvement du CH_4 et de l'éthanol. En régime transitoire, la période de récupération après les 3 cycles a nécessité 10 à 25 jours. Ce délai est relié à la présence d'éthanol dans le lixiviat. Dans un dernier temps, deux biofiltres ayant un garnissage de pierres et un garnissage mixte ont été comparés pour l'enlèvement du CH_4 et de l'éthanol présents dans un mélange gazeux en régime permanent. La section inférieure du biofiltre a permis l'élimination totale de l'éthanol. De plus, lors de l'élimination totale de l'éthanol dans la section inférieure du biofiltre, la production de dioxyde de carbone (CO_2) dépasse 16 g m^{-3} h^{-1}, pour des charges à l'entrée de CH_4 et d'éthanol de 11 et 13 g $m^{-3}h^{-1}$ respectivement. Par ailleurs, une concentration en éthanol dans le lixiviat excédant 2500 $g_{éthanol}$ $m^{-3}_{lixiviat}$ a été obtenue.

Les biofiltres ont démontré une flexibilité pour des charges par à-coups d'éthanol suivies de périodes de carence. Le principal inconvénient du biofiltre à lit de pierres par rapport au biofiltre mixte est une perte de charge élevée dans la section inférieure du biofiltre. Une période de carence est un excellent moyen de contrer la perte de charge.

Mots-clés: Biofiltre, méthane, alcool, mélange, régime transitoire

ABSTRACT

Since methane (CH_4) is a greenhouse gas with hazardous effects for global warming, every effort should be made to reduced methane emissions. Biofilters are potential candidates for CH_4 removal. In food and beverage industries as well as ethanol refineries, the feed of the biofilter might be a mixture of CH_4 emissions from wastewater treatment unit and ethanol emissions from other units. The presence of CH_4 as a mass transfer limited and ethanol vapor as a kinetic limited pollutant in a mixture can produce several limitations in a biofilter. The main objective of this research is to evaluate the limitations of CH_4 biofiltration or in the presence of ethanol vapors under steady and transient state conditions. First, a literature review was provided on mass transfer and kinetic limited organic pollutants removal in biofilters and the related limitations. Subsequently, the CH_4 elimination was assessed in a biofilter in order to evaluate the effect of CH_4 inlet concentration in the range of 1000 to 13000 ppmv and a gas flow rate of 3 L min^{-1} on the biofilter performance. A maximum CH_4 elimination capacity (EC_{max}) of 45 g m^{-3} h^{-1} was obtained for a CH_4 inlet load (IL) of 87 g m^{-3} h^{-1}. The biofilter tolerated CH_4 shock loads as well as different types of CH_4 and nutrient starvations. Subsequently, the steady state and dynamic behaviors of CH_4 elimination in the presence of ethanol vapor was studied in an inorganic bed biofilter with empty bed residence times (EBRTs) of 6, 3 and 1.5 min. Ethanol addition was performed in 3 cycles based on the EBRTs. An EBRT of 6 min with corresponding CH_4 and ethanol inlet loads of 132 and 4.5 $g_{pollutant}$ m^{-3} h^{-1} respectively, caused the least limitations for the simultaneous removal of CH_4 and ethanol in the biofilter. According to dynamic behavior of the biofilter, the recovery time after the three cycles took from 10 to 25 days. The delayed biofilter recovery was linked to the presence of ethanol in the liquid effluent. Finally, a stone-based bed and a hybrid packing biofilter were compared for CH_4 and ethanol removal in a mixture under steady and transient state conditions. Ethanol was completely removed in the bottom sections of both biofilters. A large carbon dioxide (CO_2) production rate exceeding 18 g m^{-3} h^{-1} occurred in the bottom sections for CH_4 and ethanol inlet loads of 11 and 13 g m^{-3} h^{-1} respectively. In addition, an ethanol concentration in the leachate exceeding 2500 $g_{ethanol}$ $m^{-3}_{leachate}$ was obtained for both biofilters. The biofilters were flexible to an ethanol shock load followed by a starvation period. The main drawback of the stone based bed biofilter compared to the hybrid packing biofilter was an excess pressure drop in the bottom section. Starvation was found an effective strategy for reducing the pressure drop.

Keywords: Biofilter, methane, alcohol, mixture, transient, starvation

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CHAPTER 1. Introduction

Greenhouse gas (GHG) emissions like methane (CH_4) and carbon dioxide (CO_2) are serious threats to the environment because of their impacts on climate change and global warming. Presently, there is a global consensus to reduce GHGs emissions. Recently, in Paris (2015) and in Morocco (2016) about 200 countries including Canada signed an agreement to keep the global temperature increase below 2 °C compared to pre-industrial levels [1]. Methane is the second most important GHG after CO_2 with a global warming potential (GWP) of 25 in comparison with CO_2 with a GWP of 1 [2]. Therefore, CH_4 emissions reduction is essential in order to prevent global warming. Anthropogenic activities like landfills, live stocks, wastewater treatment plants (WWTPs), coal mines and natural gas sectors contribute approximately 60% of total CH_4 emissions in the world [3]. CH_4 emissions from anthropogenic activities usually have low concentrations (<3% v/v) which might not be amenable to elimination by chemical oxidation (e.g., combustion). Nevertheless, combustion may produce secondary gaseous pollutants like nitrogen oxides (NO_x) or dioxines. If the CH_4 concentration is low (<3% v/v), biological techniques such as biofiltration can be used as an appropriate technique for CH_4 removal. Biofiltration is based on a CH_4 bioxidation in a biofilter by methanotrophs, CH_4 degrading bacteria, into CO_2, water (H_2O), biomass and salts [4]. In biofiltration, CH_4 is converted to less hazardous materials and consequently, the net GWP is reduced. Biofilters are usually cost effective and easy to operate with less production of hazardous secondary pollutants. Biofilters have been investigated for different types of gaseous pollutants emissions removals. For example, the elimination of volatile organic compounds (VOCs) (e.g., benzene, toluene), volatile inorganic compounds (VICs) (e.g., NH_3, H_2S) and some odorous pollutants like acetic acids have been studied in biofilters. In addition, several studies focused on CH_4 elimination in biofilters in order to reduce greenhouse gas emissions.

In general, pollutant mass transfer from gas into biofilm phase and kinetics of biodegradation are the two main limitations for a typical pollutant's removal in biofilters.

Methane's poor mass transfer from gas into the biofilm phase has been noted the most important limitation for CH_4 biofiltration. The effect of some operating parameters like inlet load, temperature, nutrient solution and packing materials have been studied for CH_4 biofilters in

order to improve the CH_4 elimination. Among the operating parameters, CH_4 inlet load is a key factor since it is a combination of CH_4 inlet concentration and gas flow rate. Some studies discussed about the effect of CH_4 inlet load in terms of gas flow rate variations. However, the effect of CH_4 inlet concentration at a fixed gas flow rate has received less attention. Over a range of CH_4 inlet concentration, a CH_4 biofilter can encounter with mass transfer and kinetics limitations. Therefore, it is important to determine the critical CH_4 concentration which may cause performance reduction in a biofilter. The CH_4 critical inlet concentration reveals a switching point between mass transfer and kinetic limitations.

In industrial sectors responsible for CH_4 emissions, CH_4 is frequently present in a mixture with other kinds of gaseous pollutants like volatile fatty acids (e.g., acetic acid), chloromethane, toluene and alcohols. In food and beverage industries or refineries, CH_4 can be in a mixture with ethanol vapors. In the mentioned industries, ethanol emission from different units might be mixed with CH_4 emissions in order to be fed to the waste gas treatment unit.

Ethanol vapors are present in approximately 5% of total CH_4 emissions in the world [2]. Biofilters have been used for ethanol vapors elimination in a few studies. Ethanol vapor is totally different from CH_4 in terms of water solubility and mass transfer limitations from gas into the biofilm phase. Ethanol miscibility with water guarantees an enhance ethanol mass transfer from gas to biofilm phase. Because of ethanol's low dimensionless Henry's constant of 0.002 (at 25 $^{\circ}$C, P=1 atm) [5], fewer mass transfer limitations are produced for ethanol from gas into biofilm phase. On the other hand, the CH_4 mass transfer from gas into the biofilm phase is poor because of high CH_4 dimensionless Henry's constant of 28 at 25 $^{\circ}$C, P=1 atm [6]. In addition, ethanol is more biodegradable than CH_4. However, the excess solubility of ethanol in the biofilm phase may cause toxicity problems for microorganisms present in the biofilm phase. Therefore, the presence of ethanol vapors during CH_4 biofiltration is hypothesized to produce a variety of challenges and limitations in terms of mass transfer and kinetics of biodegradation. In this regard, some operating parameters like empty bed residence time (EBRT) or filter bed packing are expected to have opposite impacts on the removal of each pollutant. For example, a suitable packing material or an appropriate EBRT range for ethanol removal in biofilters may limit the CH_4 removal at the same time when both pollutants are present. Therefore, more studies on operating parameters like EBRT and filter bed should be performed in order to reduce the limitations when both pollutants are present in a biofilter.

Methane biofiltration has been usually carried out under steady state conditions. Nevertheless, according to the industrial application of biofilters for CH_4 removal, different transient conditions can occur. The ability of CH_4 biofilters to deal with transient conditions can provide valuable information for plant managers and researchers who worked with pilot or full field scale CH_4 biofilters. Sudden variation of pollutants inlet concentration or gas flow rate, shutdown during weekends or maintenance periods and the periodic presence of a second pollutant are common situations for industries with CH_4 emissions. For example, CH_4 shock load, CH_4 or nutrient starvations and the intermittent load of alcohols (in a mixture with CH_4) are common transient conditions for the biofilters. The transient conditions are usually harsh situations for biofilters. In this regard, biofilters are supposed to withstand the transient conditions. Therefore, the biofilter performance over transient conditions in terms of biofilter flexibility and sensibility is important. The biofilter response to transient conditions is expected to be quick and the recovery time for restoration after the harsh condition should be short. In addition, the study of dynamic behaviors of CH_4 biofilters during transient conditions will give a better understanding about the important phenomena of the process.

To the author's best knowledge, no study discussed the effect of CH_4 inlet concentration in terms of mass transfer and kinetic limitations as well as the critical inlet concentration responsible for the biofilter performance reduction. In addition, presence of an alcohol vapor like ethanol in a CH_4 biofilter and the associated limitations in terms of mass transfer and kinetic limitations has never been investigated. Moreover, no study discussed the effect of different transient conditions for a CH_4 biofilter in terms of transient loads, shock loads, intermittent loading of a second pollutant, shutdown periods and starvations.

The general objective of this study was to investigate the steady and transient state performance of biofilters for CH_4 removal solely and in the presence of ethanol vapors. This study carried out under three specific objectives. The first specific objective was to evaluate a CH_4 biofilter performance under steady and transient state conditions. The effect of CH_4 inlet concentration was investigated under steady state conditions. Accordingly, different strategies of transient conditions in terms of shock loads, nutrient starvations and shutdowns were applied to the CH_4 biofilter in order to evaluate the biofilter's ability to encounter with transient conditions.

The second objective was to evaluate a CH_4 biofilter in the presence of ethanol vapor under steady state and transient state conditions. In this regard, the effect of gas flow rate or EBRT, was evaluated in a CH_4 biofilter in the periodic presence of ethanol. Accordingly, the transient conditions and the sensitivity of the biofilter under the intermittent ethanol addition at different EBRTs were discussed.

The third objective was to evaluate a stone-bed and a hybrid packed bed biofilter for CH_4 elimination in the absence and presence of ethanol vapor under steady state and transient state conditions. The effect of stepwise ethanol concentration increases was studied under steady state condition in the biofilters. Accordingly, transient conditions in the forms of ethanol shock loads and shutdown periods were applied to the biofilters and the biofilters ability to tolerate the transient conditions were examined.

This thesis contains 6 chapters including 1 review article and 3 research articles.

Chapter 1 is an introduction to topic of the thesis. This chapter presents a general statement about the topic, the questions and problems related to the issue and objectives of the project.

Chapter 2 presents a literature review on two groups of organic gaseous pollutants as mass transfer limited (e.g., CH_4) and kinetic limited (e.g., ethanol). Each group of the pollutant is defined in this chapter. The abatement of the mention pollutants in biofilters and biotrickling filters and the effect of several important operating parameters under steady or transient state condition are discussed. In addition, the limitations and challenges when both types of pollutants are present in a mixture are evaluated. Finally, some improved bioprocesses to reduce the mass transfer and kinetic limitations are introduced.

Chapter 3 presents CH_4 biofiltration under steady state and different transient state conditions. The steady state performance of the CH_4 biofilter is evaluated over a range of inlet concentrations. Moreover, the biofilter dynamic behavior under different transient conditions in the forms of shock loads or starvations are discussed.

Chapter 4 and 5 are dedicated to CH_4 and ethanol biofilter in a mixture. Chapter 4 presents the performance of a CH_4 biofilter under periodic ethanol additions. The dynamic behavior of the biofilter are evaluated over 3 cycles of ethanol addition corresponding to 3 different EBRTs.

The sensitivity of the CH_4 biofilter to ethanol addition as well as its recovery after ethanol completion are discussed.

Chapter 5 presents an evaluation and comparison of two different biofilters in their bottom sections for CH_4 removal in the presence of ethanol under steady and transient state conditions. Under steady state condition, the biofilters are analyzed in terms of CH_4 or ethanol removal, carbon dioxide production and pressure drop in different sections of the column. In addition, the ability of the biofilters to deal with harsh transient conditions such as shock loads and starvations are discussed.

Chapter 6 is the conclusion of the thesis including the general findings of the project. The research questions and problems are restated and discussed in this chapter.

1.1 Introduction in French

Les émissions de gaz à effet de serre (GES) tel que le méthane (CH_4) et le dioxyde de carbone (CO_2) sont de réelles menaces pour l'environnement en raison de leurs impacts sur le changement climatique et le réchauffement climatique. Le méthane est le deuxième GES le plus important après le CO_2 avec un potentiel de réchauffement planétaire (PRP) 25 fois plus élevé que celui du CO_2. Les activités anthropiques telles que les décharges, l'élevage, les stations d'épuration des eaux usées, les mines de charbon et l'industrie du gaz naturel contribuent pour environ 60% des émissions totales de CH_4 dans le monde. Les émissions de CH_4 provenant d'activités anthropogéniques ont généralement de faibles concentrations (<3% v/v) qui ne pourraient pas être éliminées par oxydation chimique (par exemple, la combustion). Dans les cas de faibles concentrations de CH_4 (<3% v/v), des procédés biologiques tels que la biofiltration peuvent être utilisées pour l'élimination du CH_4. La biofiltration est basée sur une bioxydation du CH_4 dans un biofiltre par des méthanotrophes, bactéries transformant le CH_4, en CO_2, en eau (H_2O), en biomasse et en sels. Dans la biofiltration, le CH_4 est transformé en composés moins dangereux et par conséquent, le PRP net est réduit. Le faible transfert de masse du CH_4 à l'intérieur du biofilm a été noté comme la limitation la plus importante lors de la biofiltration du CH_4.

Dans les secteurs industriels responsables des émissions de CH_4, ce dernier est souvent présent en mélange avec d'autres types de polluants gazeux tels que des acides gras volatils (par exemple, l'acide acétique), du chlorométhane, du toluène ou des alcools. Dans les industries

alimentaires ou les raffineries, le CH_4 peut se trouver en mélange avec des vapeurs d'éthanol. Les vapeurs d'éthanol sont présentes dans environ 5% des émissions totales de CH_4 dans le monde. La présence de vapeurs d'éthanol lors de la biofiltration du CH_4 pourrait produire une variété de défis et de limites en termes de transfert de masse et de cinétique de biodégradation. La biofiltration du CH_4 a été habituellement effectuée en régime permanent. Néanmoins, lors de l'application industrielle des biofiltres pour l'élimination du CH_4, différentes conditions transitoires peuvent survenir. La performance des biofiltres de CH_4 en conditions transitoires peut fournir des informations précieuses pour les responsables de l'usine et les chercheurs œuvrant avec des biofiltres de CH_4 à l'échelle pilote ou à l'échelle industrielle. La variation soudaine de la concentration d'entrée des polluants ou du débit de gaz, l'arrêt pendant les fins de semaine ou lors de périodes de maintenance et la présence périodique d'un deuxième polluant sont des situations courantes pour les industries ayant des émissions de CH_4. À la meilleure connaissance de l'auteur, aucune étude n'a préalablement discuté de la présence de vapeur d'alcool comme de l'éthanol dans un biofiltre de CH_4 ainsi que des limitations associées. En outre, aucune étude n'a discuté de l'effet de différentes conditions transitoires pour un biofiltre de CH_4 en termes de charges transitoires, de charges par à-coups, de chargement intermittent d'un deuxième polluant, de périodes d'arrêt. L'objectif général de cette étude était d'étudier la performance en régime permanent ou en régime transitoire des biofiltres pour l'élimination du CH_4 en absence ou présence de vapeurs d'éthanol.

Cette thèse contient 6 chapitres comprenant 1 article de revue et 3 articles de recherche. Le chapitre 1 est une introduction au sujet de la thèse. Le chapitre 2 présente une revue de la littérature sur deux groupes de polluants gazeux organiques, ceux pour qui leur biodégradation est limitée par le transfert de masse (tel que le CH_4) et ceux pour qui leur biodégradation est limitée par la cinétique de biodégradation (tel que l'éthanol). Le chapitre 3 présente la biofiltration du CH_4 en régime permanent sous différentes conditions d'état transitoires (par exemple, variations par à-coups, conditions de carence). Les chapitres 4 et 5 sont consacrés à la biofiltration du CH_4 et de l'éthanol présents dans un mélange. Le chapitre 4 présente la performance d'un biofiltre de CH_4 sous des ajouts périodiques d'éthanol. Le chapitre 5 présente une évaluation et une comparaison de deux biofiltres différents dans leurs sections inférieures pour l'élimination du CH_4 en présence d'éthanol en régime permanent ou en régime transitoire. Le chapitre 6 présente la conclusion de la thèse.

CHAPTER 2. Literature review

Avant propos:

L'article "Elimination of mass transfer and kinetic limited organic pollutants in biofilters: a review*"* a été publié dans le Journal "*International Biodeterioration and Biodegradation*" 119 (2017) 336-348.

TITRE: Élimination de composés organiques à limitations par transfert de masse ou par voie cinétique

Title: Elimination of mass transfer and kinetic limited organic pollutants in biofilters: a review

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Contribution to the document: This paper presented a literature review on the elimination of two pollutant's groups as mass transfer and kinetic limited in biofilters. The removal of CH_4 and ethanol as a mass transfer limited and kinetic limited pollutant respectively were discussed in this thesis. Therefore, this review paper is helpful and relevant to the thesis topic. In addition, this review paper presented the removal of mass transfer and kinetic limited pollutants under transient state conditions which is relevant to the main objective of the thesis.

Elimination of mass transfer and kinetic limited organic pollutants in biofilters: a review

2.1 Résumé

Les limitations par transfert de masse et par voie cinétique de composés gazeux sont deux contraintes lors du contrôle de polluants gazeux dans un biofiltre (BF) ou dans un biofiltre à percolation (BTF). C'est d'autant plus problématique si les deux limitations (transfert de masse et cinétique) sont présentes. Dans cet article, des composés organiques ayant des limitations par transfert de masse ou cinétique sont présentés et des études récentes sur ces composés sont passées en revue. Par la suite, les conditions opératoires les plus adéquates pour chaque type de limitations sont discutées. Pour terminer, de nouveaux bioprocédés, tels des biofiltres percolateurs avec deux phases liquides, des biofiltres avec une alimentation par étape et des biofiltres hybrides permettant de surmonter les limitations par transfert de masse ou cinétique de composés organiques sont présentés.

Mots clefs: Rejets gazeux, biofiltre, transfert de masse, cinétique, mélange de polluants, bioprocédés améliorés

2.2 Abstract

Mass transfer and kinetic limitations are two obstacles to the removal of a pollutant from the gas phase in a biofilter (BF) or a biotrickling filter (BTF). The issue becomes more challenging when mass transfer and kinetic limitations are present especially for treatment of pollutants in mixtures. In the present study, the most common organic pollutants which may have mass transfer or kinetic limitations in BFs and BTFs are described. Accordingly, the recent studies of mass transfer limited and kinetic limited organic pollutants elimination in BFs and BTFs are reviewed. Subsequently, the most effective operating parameters for each sort of limitations are discussed. Finally, some improved bioprocesses like two liquid phase biotrickling filters, step feeding and hybrid biofilters to overcome the limitations of mass transfer and kinetic limited organic pollutants are discussed.

Keywords: Waste gas, biofilter, mass transfer, kinetics, pollutants mixture, improved bioprocesses

2.3 Introduction

Gaseous emissions like volatile organic components (VOCs) (e.g., benzene, styrene) or volatile inorganic components (VICs) (e.g., hydrogen sulfide (H_2S), ammonia (NH_3)) from chemical, petrochemical, pulp and paper industries contribute to air pollution [7]. In addition, greenhouse gas emissions (GHGs) like methane (CH_4) from landfill, livestock, coal mine and wastewater treatment plants with drastic influence on climate change and global warming are also considered as air pollutants [3, 8]. In some cases, odorous components like acetic acid or ammonia (NH_3) are necessary to be removed since they have unpleasant smells [9]. Pollutant's removal from gas phase is mainly based on two techniques: 1) physico-chemical and 2) biological techniques. Adsorption, absorption, condensation, incineration and plasma are some examples of physico-chemical techniques [7, 10, 11]. Biological techniques are based on pollutant biodegradation by a microbial transformation into carbon dioxide (CO_2), water (H_2O), biomass, etc. [9]. The initial interest in biological methods for waste gas treatment arose from their promising potential of contaminants mineralization with low secondary pollutions and disposals unlike what usually happens with other physico-chemical methods [9]. Biofilter (BF), biotrickling filter (BTF) and bioscrubber are the main types of bioreactors which have been used for bioxidation of VOCs, VICs, GHGs and odor components [12, 13]. Lab scale BFs and BTFs have been focused in several studies for pollutant inlet concentrations usually lower than 1% (v/v) and gas flow rates usually less than 1 $m^3\ h^{-1}$ [14-16]. An aqueous phase (biofilm phase) and a gas phase are in contact with each other in BFs and BTFs. Therefore, the mass transfer of a target pollutant from gas to the biofilm phase as well as the pollutant's solubility in the biofilm phase are among the concerns which may affect the BF's performance [17]. For example, mass transfer limitations from gas to the biofilm phase in BFs and BTFs for pollutants like CH_4, ethylene (C_2H_4), n-hexane, toluene, styrene, xylene and α-pinene could be as a result of poor pollutant solubility in the biofilm phase (<500 g m^{-3}_{Liq} at 25 ˚C and 1 atm), high dimensionless Henry's law constant (>0.1 at 25 ˚C and 1 atm) or high vapor pressure (>5000 kPa at 25 ˚C) [18]. In contrast, components with less mass transfer limitations like alcohols, volatile fatty acids (VFAs) and ketones can be limited by the kinetics of biodegradation. In this regard, the high concentration of pollutants in the biofilm phase may increase the risk of toxicity for the

biocatalysts or cause excess biomass growth and pressure drop [9]. A number of studies including review articles discussed the performances of BFs and BTFs as well as operating parameters (filter bed, temperature, moisture content, etc) while paying less attention to the nature of the limitations in terms of mass transfer or kinetics [12, 15, 19].

In this study, two groups of organic pollutants described as mass transfer limited and kinetic limited were selected. Subsequently, a literature review was made discussing about BFs and BTFs performance implemented for each group of pollutants usually in the last 10 years. In addition, the operating parameters that could cause problems for each group of pollutants were analyzed. Finally, the applications and limitations of BFs and BTFs for a mixture of both groups of pollutants were investigated. In this regard, some improved designs and configurations of BFs for treating simultaneously both types of the pollutants were reviewed.

2.4 Biofilter (BF) and biotrickling filter (BTF)

In recent years, conventional BFs have been used as the primary bioreactor configuration for waste gas biotreatment, odor removal or even as a secondary treatment stage after physical-chemical oxidation [14, 15]. In lab scale BFs, a contaminated and humidified air stream is passed through a packed bed column which has been enriched by appropriate biocatalysts [9]. In the presence of oxygen, an organic pollutant, as a substrate, is biodegraded. Thus, the pollutant is converted to less hazardous materials such as CO_2, H_2O and biomass [9]. The gas flow direction in a BF or BTF can be upward or downward. A solution is frequently supplied to BFs in order to provide sufficient macro and micro nutrients like nitrogen, phosphorous and potassium for the biocatalysts. Figure 2.1 shows the main phenomena which occur during biofiltration. The pollutant biodegradation happens in an aqueous phase (biofilm phase). Therefore, mass transfer of pollutants from gas to liquid phase (biofilm phase) and biodegradation of the pollutant in the biofilm phase by the biocatalysts are the two main limitations for the elimination of gaseous pollutants in biofiltration [17]. The main difference between BFs and BTFs is the presence of a recirculating liquid phase in BTFs. The thickness of the biofilm phase in BFs is small enough to enhance the mass transfer of pollutants from gas into the biofilm phase [17]. The main drawback of BFs is the accumulation of biomass due to the lack of a mobile liquid phase. The mobile aqueous phase in BTFs provides an extra layer of liquid around the biofilm and represents a barrier to contaminant's mass transfer [17]. However, the mobile liquid phase in BTFs makes the control of operating parameters like pH, temperature, water content and nutrient

solution easier. For instance, for treatment of H_2S with the potential of acidification, the mobile liquid phase ensures the neutral condition by the addition of buffering materials to the storage tank of recirculation liquid [12].

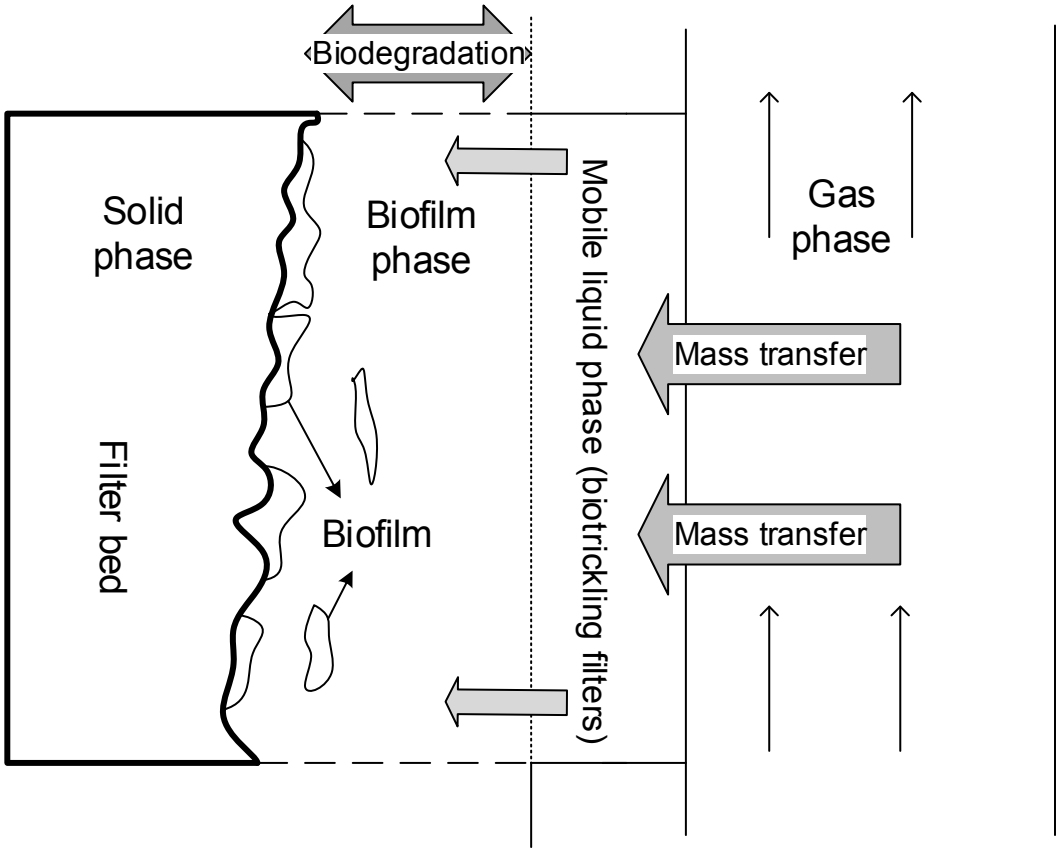

Figure 2.1: The main phenomena and limitations in biofiltration and biotrickling filtration

2.4.1 Performance parameters

The performance of BFs and BTFs can be illustrated by different parameters [15]:

Removal efficiency (RE)	$\frac{(C_{Gi} - C_{Go})}{C_{Gi}} \times 100$	(%)
Inlet load (IL)	$\frac{Q \times C_{Gi}}{V_f}$	(g m^{-3} h^{-1})
Elimination capacity (EC)	$\frac{(C_{Gi} - C_{Go}) \times Q}{V_f}$	(g m^{-3} h^{-1})

C_{Gi} and C_{Go} are the inlet and outlet pollutant concentrations (g m^{-3}) respectively. Q is the gas flow rate (m^3 h^{-1}) and V_f (m^3) is the volume of the biofilter.

2.5 Classification of organic pollutants based on their mass transfer and kinetic limitations

Different categorizations of organic pollutants have been suggested based on chemical structures of the components in order to be removed in BFs and BTFs [20]. However, classification of pollutants due to different resistances they meet in their biodegradation in a BF or BTF gives a better understanding of the limitations [20, 21]. According to Figure 2.1, pollutant's mass transfer from gas phase to the biofilm phase and kinetics of biodegradation are the two most important sorts of limitations in a biofilter. Therefore, a typical organic pollutant in a biofilter with limitations of elimination in terms of mass transfer from gas to the liquid phase is a mass transfer limited pollutant. On the other hand, a typical organic pollutant which is a potential candidate to cause kinetic limitations (e.g., inhibition, toxicity) in a biofilter is a kinetic limited pollutant. Mass transfer and kinetic limited pollutants are defined by the pollutants bioavailability in the biofilm phase in a pseudo gas-liquid equilibrium in a biofilter [17, 22]. In this regard, mass transfer limitation results in a limited bioavailability of a typical mass transfer limited pollutant in the biofilm phase. However, excess bioavailability of a kinetic limited pollutant in the biofilm phase ends up to kinetic limitations in terms of inhibition or toxicity. The bioavailability of a typical organic pollutant can be determined by a gas-liquid equilibrium equation (Henry's law constant), chemical structure of a pollutant (solubility and miscibility with water) and the state of the pollutant (gaseous or liquid). Table 2.1 shows a classification on the contaminants bioavailability (in the biofilm phase) basis. Physical-chemical properties of the pollutants in terms of water solubility, dimensionless Henry's law constant and vapor pressure at 25 ˚C and 1 atm are listed. According to Table 2.1, gaseous alkanes and alkenes like CH_4 and C_2H_4, liquid alkanes like n-hexane and n-pentane, liquid alkenes like α-pinene and some aromatics like toluene, styrene and xylene are examples for mass transfer limited pollutants. Basically, for mass transfer limited pollutants, poor solubility in water lower than 500 g m^{-3} results in high dimensionless Henry's law constants (>0.1) and could decrease the availability of the pollutants in the biofilm phase. Furthermore, vapor pressures higher than 5000 kPa at 25 ˚C could also diminish the chance of pollutant remaining in the biofilm phase for gaseous pollutants like CH_4 and C_2H_4. In this regard, bioelimination of gaseous pollutants like CH_4 or C_2H_4 might be limited not only by their high Henry's law constant (>0.1) but also by their high vapor pressure at ambient temperature (>5000 kPa at 25 ˚C).

Table 2.1: Physical-chemical properties of mass transfer limited and kinetic limited organic pollutants at 25 ˚C[a]

Pollutant type	**Pollutant group**	**Pollutant**	**Pollutant phase**	**Water solubility ($g\ m^{-3}$)**	**Dimensionless Henry's constant**	**Vapor pressure (kPa)**
Mass transfer limited	Gaseous alkanes	Methane	Gas	24	28	27260
	Gaseous alkenes	Ethylene	Gas	131	9	6070
	Liquid alkanes	n-pentane	Liquid	39	52	68
		n-hexane	Liquid	10	70	20
	Liquid alkenes	α-pinene	Liquid	470	0.272	4
	Aromatics	Toluene	Liquid	310	0.113	0.9
		Styrene	Liquid	180	0.25	1
		Xylene	Liquid	18	6	60
Kinetic limited	Alcohols	Methanol	Liquid	Miscible	0.0016	16
		Ethanol	Liquid	Miscible	0.002	7
		Propanol	Liquid	Miscible	0.00028	3
		n-butanol	Liquid	70000	0.000325	1
	Volatile fatty acids (VFAs)	Acetic acid	Liquid	Miscible	0.0000122	2
		Butyric acid	Liquid	Miscible	0.00002	0.1
		n-valeric acid	Liquid	24000	0.00002	0.04
	Ketones	Methyl ethyl ketone (MEK)	Liquid	256000	0.002	13
		Acetone	Liquid	Miscible	0.00136	30

[a] (Carro, 2014; Dean, 1999; Mackay et al., 2006; Staudinger and Roberts, 1996) [5, 6, 23, 24]

Therefore, if a typical component is biodegradable enough by a specific type of microorganism, mass transfer and solubility limitations may hamper its bioavailability in the biofilm phase and could influence the conversion of the pollutant [17].

Pollutants with high ability to transfer into the biofilm phase like alcohols (e.g., methanol, ethanol, propanol and n-butanol), VFAs (e.g., acetic acid, butyric acid and n-valeric acid) and ketones (e.g., acetone, methyl ethyl ketone (MEK)) are categorized as kinetic limited pollutants. According to Table 2.1, the kinetic limited pollutants with low dimensionless Henry's law constants (<0.1) and vapor pressures lower than 30 kPa (T=25 ˚C) are almost miscible with water. Therefore, the kinetic limitations like toxicity and inhibition for the biocatalyst could happen in the removal of the component in BFs and BTFs [21, 25]. Regardless of Henry's law constant, the excess bioavailability of some liquid VOCs like alcohols might be as a result of their complete miscibility with water according to their chemical structures.

Therefore, mass transfer limited pollutants are generally hydrophobic or gaseous pollutants and their removal in BFs are limited by mass transfer from gas to the biofilm phase. On the other hand, kinetic limited pollutants are generally hydrophilic pollutants or miscible components with water.

2.5.1 Biofiltration and biotrickling filtration of mass transfer limited pollutants

Figure 2.2 shows three typical trends of EC as a function of IL in BFs for mass transfer and kinetic limited pollutant removal. A maximum elimination capacity (EC_{max}) is the maximum capacity of a BF to remove a pollutant which usually occurs at a specific IL. According to Figure 2.2, the EC_{max}s at graphs A and B, correspond to the maximum ILs whereas at graph C, the corresponding IL for the EC_{max} is lower than the maximum IL. The RE_{max}s are the maximum removal efficiencies and correspond to the point with least deviations from 100% RE line. It should be pointed out that RE_{max}s do not necessarily correspond to EC_{max}s. A critical IL ($IL_{critical}$) in BFs is the maximum IL for a typical pollutant in which a complete removal (RE of 100%) can be obtained. For ILs exceeding $IL_{critical}$, the performance of BFs in terms of REs starts to decrease. Therefore, $IL_{critical}$ is a threshold for BFs in order to be under a safe operating regime.

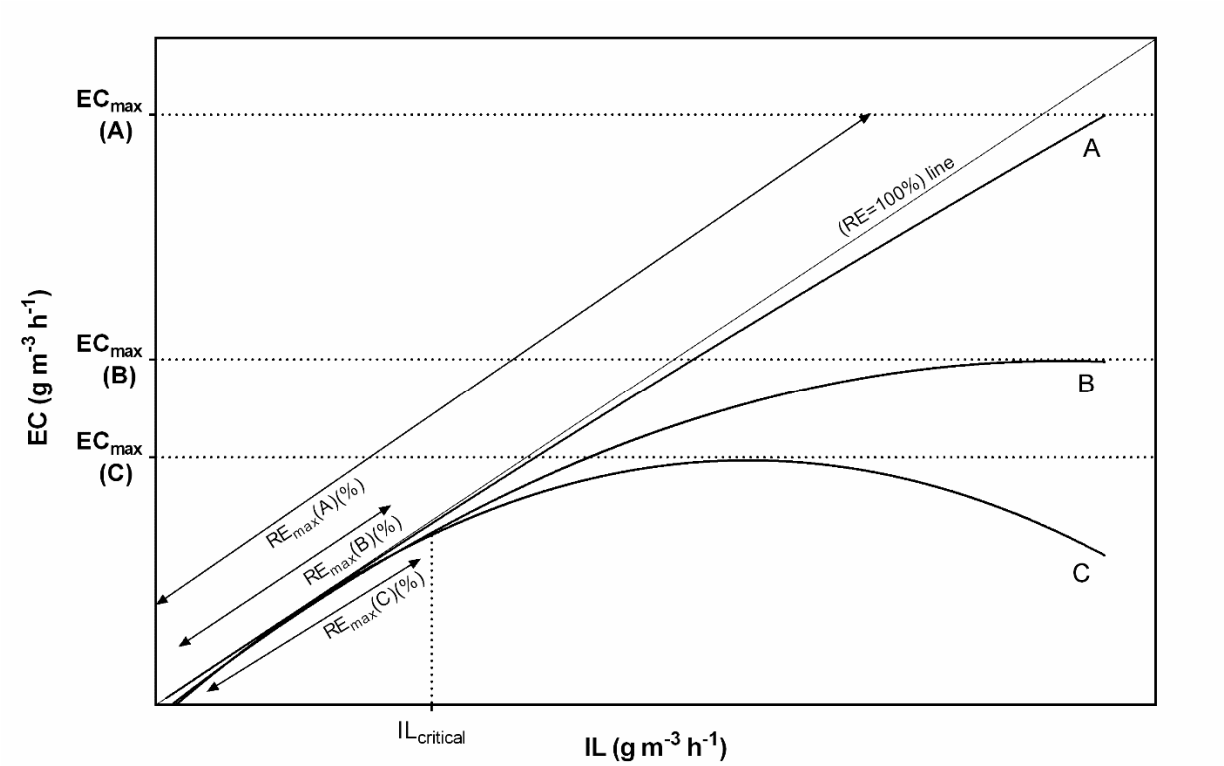

Figure 2.2: Three typical examples (A, B and C) of BF performances (EC vs. IL) for mass transfer and kinetic limited pollutants removal.

Table 2.2 presents the BFs performance to eliminate mass transfer limited pollutants at RE_{max}s as well as EC_{max}s. The studies were carried out in lab scale BFs with different packing materials and no cell immobilization. The RE_{max}s of gaseous alkanes like CH_4 were noticeably far from 100% for ILs in the range of 17 to 160 g m^{-3} h^{-1} either in BFs or BTFs. The poor performance of CH_4 BFs were attributed to poor mass transfer of CH_4 from gas to the biofilm phase [26]. The CH_4 mass transfer could be more limited in BTFs due to the presence of the recirculating liquid phase [27]. Therefore, the CH_4 RE_{max}s were usually lower in BTFs than BFs. According to Table 2.2, for CH_4 BFs, the RE_{max}s were in the range of 30 to 62% for corresponding ILs from 17 to 75 g m^{-3} h^{-1} while in CH_4 BTFs the RE_{max}s were in the range of 16 to 40% for corresponding CH_4 ILs ranging from 160 to 67 g m^{-3} h^{-1} respectively [28, 29].

According to Table 2.2, the CH_4 EC_{max}s were lower than 30 g m^{-3} h^{-1} for ILs up to 160 g m^{-3} h^{-1} for BFs and BTFs. For gaseous alkenes like C_2H_4, the RE_{max}s were 80 and 90% for corresponding ILs of 3 and 1 g m^{-3} h^{-1} in a BF and a BTF respectively. The EC_{max}s of C_2H_4 were lower than 10 g m^{-3} h^{-1} for corresponding IL of 14 g m^{-3} h^{-1}.

According to Table 2.2, for liquid alkanes, alkenes and aromatics removals in BFs and BTFs, RE_{max}s generally exceeding 95% could be reachable for corresponding ILs lower than 100 g m^{-3} h^{-1}. Table 2.2 also shows EC_{max}s over 50 g m^{-3} h^{-1} for ILs exceeding 100 g m^{-3} h^{-1} for liquid alkanes and aromatics eliminations in BFs and BTFs (for most of the studies). The vapor pressures of liquid alkanes, alkenes and aromatics (< 20 kPa at 25 ˚C) are lower than CH_4 and C_2H_4 (27260 and 6070 kPa at 25 ˚C respectively). Therefore, liquid alkanes, alkenes and aromatics are more capable of remaining in the biofilm phase compared to gaseous alkanes and alkenes. Thus, the pollutant mass transfer from gas to the biofilm phase for liquid alkanes like n-pentane and n-hexane, liquid alkenes like α-pinene and aromatics like toluene, styrene and xylene could cause less limitations compared to gaseous alkanes and alkenes (CH_4 and C_2H_4). According to Table 2.2, there was no particular difference between BFs or BTFs for most of liquid alkanes and aromatics in terms of RE_{max}s and EC_{max}s. However, for liquid alkenes removal like α-pinene, enhanced performance parameters (RE_{max}s and EC_{max}s) were obtained for a BF compared to a BTF. For example, Langolf and Kleinheinz (2006) [30] obtained a RE_{max} of 100% for α-pinene ILs up to 100 g m^{-3} h^{-1} in a BF. Nevertheless, Montes et al. (2015) [31] reached a RE_{max} of 100% in α-pinene BTF for lower ILs (ILs up to 23 g m^{-3} h^{-1}). Due to the lack of recirculation liquid phase in the BF, the mass transfer of *α*-pinene from gas to the biofilm could be enhanced [17].

Table 2.2: Removal of mass transfer limited pollutants in BFs and BTFs

Pollutant group	Pollutant	Bioreactor	Filter bed	Performance at RE_{max}		Performance at EC_{max}		References
				IL ($g\ m^{-3}\ h^{-1}$)	RE_{max} (%)	IL ($g\ m^{-3}\ h^{-1}$)	EC_{max} ($g\ m^{-3}\ h^{-1}$)	
Gaseous alkanes	CH_4	BF	Inert material	70-75	40	75	29	[32]
	CH_4	BF	Mixture of Wood chips, perlite, compost	18	62	18	11	[26]
	CH_4	BF	Coal	17	30	139	27	[33]
	CH_4	BF	Mixture of bark chips, perlite, compost	17	26	85	21	[34]
	CH_4	BTF	Polyurethane foam	160	16	160	26	[28]
	CH_4	BTF	Stone	67	40	67	25	[29]
	CH_4	BTF	Polyethylene rings	3	50	23	6	[35]
Gaseous alkenes	C_2H_4	BF	Perlite	<3	80	14	7	[36]
		BTF	Perlite	<1	90	13	9	[37]
Liquid alkanes	n-pentane	BF	Perlite	33	100	300	100	[38]
	n-hexane	BF	Compost	100	100	600	400	[39]
		BTF	Polyurethane	30-42	84	108	45	[40]
Liquid alkenes	α-pinene	BF	Lava rock	<100	100	100	100	[30]
		BTF	Lava rock	<23	100	57	25	[31]
Aromatics	Toluene	BF	Tree bark	80	98	80	80	[41]
		BF	Lava rock	<19	100	150	80	[42]
		BF	Polyurethane foam	<70	100	120	80	[43]
		BTF	Synthetic	<70	100	290	200	[44]
	Styrene	BF	Peat	20-45	95	173	81	[45]
		BTF	Polyurethane sponge	65	87	200	165	[46]
	Xylene	BF	Sugar bagasse	4	95	100	60	[47]
		BTF	Inorganic	100	93	100	93	[48]

2.5.2 Biofiltration of kinetic limited pollutants

Table 2.3 presents BFs and BTFs performance for kinetic limited pollutants like alcohols (e.g., ethanol, methanol and n-propanol), VFAs (e.g., acetic acid and butyric acid) and ketones (e.g., MEK and acetone). According to Table 3, RE_{max}s exceeding 95% could be obtained for ILs higher than 94 g m^{-3} h^{-1} in BFs and BTFs. For example, complete removal of methanol was reached in a BTF for an IL of 250 g m^{-3} h^{-1} [49] or in a BF with corresponding methanol IL of 290 g m^{-3} h^{-1} [50]. Sheridan et al. (2003) [51] reported complete elimination of n-butyric acid in a BF for an IL of 230 g m^{-3} h^{-1} [51].

According to Table 2.3, unlike mass transfer limited pollutants, BTFs for kinetic limited pollutants might provide an improved performance comparing with BFs. For instance, Ramirez-Lopez et al. (2010) [52] obtained a RE_{max} of 100% in a BF for methanol ILs lower than 125 g m^{-3} h^{-1} and Avalos Ramirez et al. (2009) [49] obtained a methanol RE_{max} of 95% in a BTF for ILs up to 250 g m^{-3} h^{-1}. For complete ethanol removal, the corresponding IL of 200 g m^{-3} h^{-1} in a BTF [53] was twice as high as in a BF [54]. Table 2.3 also provides EC_{max}s for kinetic limited pollutants. For alcohol BFs, the EC_{max}s were in the range of 100 to 1400 g m^{-3} h^{-1} for corresponding ILs from 150 to 2000 g m^{-3} h^{-1} which was 4 times higher than for other pollutants like VFAs and ketones. According to Table 2.3, BTFs usually resulted in higher EC_{max}s compared to BFs. For example, EC_{max}s of 2160 and 970 g m^{-3} h^{-1} were obtained for corresponding methanol and ethanol ILs of 3700 and 1610 g m^{-3} h^{-1} [49, 53] in BTFs which were almost twice as high as in BFs. A few studies compared a BF and a BTF for a target kinetic limited pollutant. Morotti et al. (2011) [55] compared a BF and a BTF for ethanol vapor removal and obtained similar EC_{max}s as 46 g m^{-3} h^{-1} for IL of 55 g m^{-3} h^{-1} for both configurations. Dissolving of kinetic limited pollutants like alcohols in biofilm phase could be toxic for biocatalysts [21]. For example in a methanol BF, the minimum IL which caused toxic impact and decreased the RE was reported as 300 g m^{-3} h^{-1} [50]. Transient conditions in the forms of shock loads or starvations are common situations in BFs according to their industrial applications [56].

Table 2.3: Removal of kinetic limited pollutants in BFs and BTFs

Pollutant group	Pollutant	Bioreactor	Packing materials	Performance at RE_{max}		Performance at EC_{max}		References
				IL (g m^{-3} h^{-1})	RE_{max} (%)	IL (g m^{-3} h^{-1})	EC_{max} (g m^{-3} h^{-1})	
Alcohols	Methanol	BF	Peanut shells	<125	96	2007	1438	[52]
	Methanol	BF	Lava rock	<290	100	420	310	[50]
	Methanol	BTF	Polypropylene spheres	<250	100	3700	2160	[49]
	Ethanol	BF	Sugar cane bagasse	94	100	154	107	[54]
	Ethanol	BTF	Polypropylene spheres	<250	100	1610	970	[53]
	n-propanol	BF	Compost–woodchip	2-85	100	760	600	[57]
Volatile fatty acids (VFAs)	Acetic acid	BF	Lava rock	<120	100	120	120	[58]
	Butyric acid	BF	Wood chips	<230	100	230	230	[51]
Ketones	MEK	BF	Fern chips	<115	91	115	105	[59]
	Acetone	BF	Ceramic	30-90	97	350	300	[60]
	Acetone	BTF	Polypropylene rings	<45	90	110	55	[61]

Biofilters for kinetic limited pollutants removal successfully tolerated shock loads in terms of inlet concentration sudden variation. Rene et al. (2010) [62] applied a methanol shock load from 60 to 250 g m^{-3} h^{-1} (inlet concentration from 1.5 to 5 g m^{-3}) for 8 hours and observed a methanol RE reduction from 100 to 70%. The promising tolerability of kinetic limited pollutants BFs to shock loads might be addressed to the enhanced bioavailability of kinetic limited pollutants in the biofilm phase. In this regard, the biofilm phase might play as a reservoir to absorb the kinetic limited pollutant immediately in order to degrade it gradually. The recovery of the BF in terms of methanol RE, when the methanol IL restored to the initial value (60 g m^{-3} h^{-1}) was instantaneous. However, the recovery of kinetic limited pollutants BFs after a shock load can be delayed because of the excess presence of the kinetic limited pollutant in the biofilm phase. A slight reduction of RE from 100 to 94% was observed for a methanol BTF when the IL suddenly increased from 50 to 600 g m^{-3} h^{-1} for 5 hours at a constant EBRT of 26 s [63]. Nevertheless, a significant methanol RE reduction of 25% occurred after a shock load while the methanol IL brought back to 50 g m^{-3} h^{-1}. This reduction was attributed to the presence of methanol with corresponding concentration of 3000 g m_{iquid}^{-3} in the liquid phase of the BTF.

2.6 Important parameters for mass transfer and kinetic limited pollutants removal in BFs and BTFs

2.6.1 Support media

Packing materials should provide an adequate environment for microorganisms to grow and perform biological activities [7, 64]. Many factors like specific surface area, moisture holding, low density and tendency to compact, adsorption properties and nutrient supply determine the characteristics of a proper material to be used in a BF or BTF [65]. Biotrickling filters are filled with inert packing materials like perlite, lava rock, ceramic, granular activated carbon (GAC), polyurethane foam and polypropylene spheres [53, 66-69] while BFs are frequently filled with organic packing materials such as soil, compost, peat, leaves and wood chips [70-74] or a mixture of organic and inorganic packing [75, 76]. Table 2.4 presents the effect of bed materials on the BF and BTF performance for mass transfer limited pollutants removal.

Table 2.4: Mass transfer limited pollutants removal in BFs with different packing materials

Pollutant	Packing material	Particle size (mm)	Specific surface area	IL, EC ($g\ m^{-3}\ h^{-1}$) and RE (%)	References
CH_4	Sponge-based	25	Not reported	IL=20 EC=3 RE=15	[4]
	Blast furnaces slag	10	Not reported	IL=20 EC=4 RE=20	
	Expanded vermiculite	6	Not reported	IL=20 EC=6 RE=30	
CH_4	Expanded clay	7	470 $m^2\ m^{-3}$	IL=90 EC=15 RE=16	[77]
	Rock	5	1250 $m^2\ m^{-3}$	IL=90 EC=40 RE=45	
	Rock	2	1360 $m^2\ m^{-3}$	IL=90 EC=50 RE=55	
Toluene	Compost-organic binder (90/10 v/v)	5 10 20	590 $m^2\ m^{-3}$ 280 $m^2\ m^{-3}$ 120 $m^2\ m^{-3}$	EC_{max}=180 EC_{max}=90 EC_{max}=45	[78]
Styrene	GAC	4	Not reported	IL=22 EC=20 RE=90	[79]
	Perlite	2	Not reported	IL=22 EC=10 RE=45	
Styrene	Peat	Not reported	13.4 $m^2\ g^{-1}$	IL=90 EC=60 RE=65	[80]
	Coconut fiber	Not reported	0.9 $m^2\ g^{-1}$	IL=90 EC=40 RE=45	

The target pollutant may restrict the selections for an appropriate packing material. For mass transfer limited components removal in BFs, high specific surface area as well as adsorption properties of the packing material may support the mass transfer of the pollutant [15, 64]. Nikiema and Heitz (2010) [77] compared 3 organic packing materials for CH_4 biofiltration. When the specific surface area of the packing materials increased from 470 to 1360 $m^2\ m^{-3}$, they observed an EC improvement from 15 to 50 $g\ m^{-3}\ h^{-1}$ for a CH_4 IL of 90 $g\ m^{-3}\ h^{-1}$. Delhoménie et al. (2002) [78] studied the characteristics of 3 different compost-organic binder packing materials for toluene BFs. They obtained ECs of 180, 90 and 45 $g\ m^{-3}\ h^{-1}$ for pellets with specific surface area of 590, 280 and 120 $m^2\ m^{-3}$ respectively for IL variation from 100 to 216 $g\ m^{-3}\ h^{-1}$. Thus, the ECs were approximately improved linearly when the pellets specific surface area increased. A comparison of peat and coconut fiber as support media with corresponding specific surface area of 13.4 and 0.9 $m^2\ g^{-1}$ for styrene biofiltration was performed by Perez et al. (2014) [80]. The peat-based biofilter showed a higher EC of 60 $g\ m^{-3}\ h^{-1}$ compared to the coconut fiber biofilter with an EC of 45 $g\ m^{-3}\ h^{-1}$ for a constant IL of 90 $g\ m^{-3}\ h^{-1}$ possibly due to its higher specific surface area. Paca et al. (2009) [79] compared two BFs with GAC and perlite as filter beds respectively for styrene elimination. They obtained an EC of 20 $g\ m^{-3}\ h^{-1}$ for the BF with GAC versus an EC of 10 $g\ m^{-3}\ h^{-1}$ in the perlite BF for an IL of 22 $g\ m^{-3}\ h^{-1}$ due to high adsorption properties of GAC compared to perlite.

It should be pointed out that packing materials with high density and tendency to compact with small pore size like raw materials compost may result in excess pressure drop [15, 64, 66]. Some studies on BFs of kinetic limited pollutants like ethanol and MEK [53, 81] reported excess biomass production. Excess biomass production in kinetic limited pollutants BFs might cause problems such as clogging, channeling and high pressure drop [82]. Ryu et al. (2010) [83] observed a linear pressure drop increase from 1 to 100 $mmH_2O\ m_{bed}^{-1}$ for a benzene BF packed with polyurethane foam while the biomass concentration increased from 0.8 to 3 $g_{biomass}\ g_{bed}^{-1}$. In addition, the benzene EC decreased from 600 to 200 $g\ m^{-3}\ h^{-1}$ (IL of 600 $g\ m^{-3}\ h^{-1}$) as a result of the excess biomass accumulation. Inert and large particle packing materials like ceramic pellets provided a more even distribution of biomass [82, 84]. Morgan-Sagastume et al. (2001) [85] compared to inert porous pellets and wood chips for methanol biofiltration. For an IL of 150 $g\ m^{-3}\ h^{-1}$, the wood chips bed BF exhibited 6 fold higher pressure drop comparing with an inert bed BF (260 versus 50 $mmH_2O\ m^{-1}$). Therefore, packing materials like compost which

enhance the pollutant mass transfer for mass transfer limited pollutant may cause excess pressure drop for kinetic limited pollutants.

2.6.2 Water content

The principal role of humidification in BFs is to guarantee an aqueous phase for microorganisms [86]. In biofilters, low water content, less than 40% $w_{water} w_{packing}^{-1}$, contributed to more than 75% of operating problems such as bed drying and channeling, which are irreversible phenomena [86]. In contrast, high moisture content (>80% $w_{water} w_{packing}^{-1}$) may result in the formation of anaerobic zones and excess pressure drop [85, 86]. The optimum value of water content depends upon media composition, and operating parameters like temperature and contaminants [86, 87]. The water content in BFs is frequently set at 40-60% $w_{water} w_{packing}^{-1}$ for most of packing materials [86, 87].

For mass transfer limited pollutants, the greater amount of water available in the BFs presents a more pronounced barrier to the pollutant's mass transfer into the biofilm phase [88]. In some BFs, beside pre-humidification of the inlet air stream, a secondary humidification is performed by irrigation. This type of humidification results in a thicker biofilm layer and provides a higher mass transfer barrier for pollutants [88, 89]. Bagherpour et al. (2005) [88] reported a 20% decrease of RE for an IL of 0.1 g m^{-3} h^{-1} in an α-pinene BF with a volume of $93*10^{-4}$ m^3 when $83*10^{-5}$ m^3 water was added daily. In BTFs, liquid recirculation flow rate is a key factor either in startup period or during operation [14]. High recirculation liquid flow rates may decrease the mass transfer of mass transfer limited pollutants from gas to biofilm phase. Lee et al. (2010) [37] studied the biotrickling filtration of ethylene and demonstrated that trickling liquid flow rates higher than $5.4*10^{-3}$ m^3 h^{-1} (velocity of 0.8 m h^{-1}) diminished the surface area of the packing and caused mass transfer limitations. However, exceeding liquid trickling velocity for kinetic limited pollutants elimination in BTF may result to an enhanced pollutant mass transfer from the liquid to the biofilm phase. In addition, increasing the trickling liquid velocity can avoid liquid channeling and ends up to a more uniform water distribution in a BTF [90]. To our best knowledge, no study discussed about the effect of water content for organic kinetic limited pollutants in BFs and BTFs.

2.6.3 Temperature

Temperature is a key parameter in BFs and BTFs since it has different effects either on mass transfer of contaminant from gas to biofilm phase or on kinetics of biodegradation. The optimum temperature for BFs has been reported in the range of 15 to 30 °C either for mass transfer or kinetic limited pollutants [91-93]. According to the industrial requirements, it is hardly possible to maintain the temperature in the optimum range due to unavoidable temperature gradient between the inlet air stream and the support media or between outside temperature and the BF. Therefore, BFs and BTFs should be tolerant of low temperatures (<20 °C) or high temperatures (> 35 °C). Table 2.5 presents mass transfer and kinetic limited pollutants removal in BFs under different temperatures.

Few investigations compared the performance of a BF under mesophilic and thermophilic conditions for mass transfer and kinetic limited pollutants to verify the BF stability under harsh conditions. Mohammad et al. (2007) [93] successfully removed benzene, toluene, ethyl benzene and xylene (BTEX) vapors under mesophilic (20 °C) and thermophilic (50 °C) conditions. Depending on ILs (3-250 g m^{-3} h^{-1}), under mesophilic condition, ECs varied from 3 to 188 g m^{-3} h^{-1} with an average RE of 96%. Nevertheless, under thermophilic conditions, the EC_{max} and RE were 218 g m^{-3} h^{-1} and 83% respectively which showed a higher EC compared to the mesophilic conditions [93].

In general, increasing temperature results in increasing Henry's law constant and leads to a decrease of contaminant's solubility in the biofilm phase [18]. Thus, for mass transfer limited pollutants, rising temperature could diminish the performance of BFs and BTFs [92, 93]. Zamir et al. (2014) [94] increased the temperature of an n-hexane BF from 35 to 40 and 45 °C for an IL of 500 g m^{-3} h^{-1}. The RE consequently dropped respectively from 100 to 80% due to n-hexane mass transfer limitations and from 80 to 10% because of microbial activity reduction. However, most of the studies evaluated the global effect of the temperature on a BF performance and not exclusively on mass transfer or kinetic limitations. Ménard et al. (2011) [92] investigated the bioconversion of CH_4 in a BF in the range of 4 to 43 °C. They obtained an optimum temperature range of 30 to 34 °C with an EC of 30 g m^{-3} h^{-1} for an IL of 80 g m^{-3} h^{-1}.

Table 2.5: Mass transfer and kinetic limited pollutants removal in BFs under different temperatures

Pollutant	Temperature (°C)	IL (g m^{-3} h^{-1})	EC (g m^{-3} h^{-1})	RE (%)	References
CH_4	4	80	1	2	[92]
	14	80	10	13	
	25	80	20	25	
	30	80	25	31	
	43	80	20	25	
BTEX	20	3-250	3-188	96	[93]
	50	3-250	3-218	83	
n-hexane	35	500	500	100	[94]
	40	500	400	80	
	45	500	50	10	
Ethanol	22	230	140	60	[95]
	53	230	140	60	
Ethanol	25	170	120	70	[91]
	30	170	140	82	
	35	170	100	60	
	40	170	95	55	
n-butanol	30	156	140	90	[96]
	35	156	130	85	
	40	156	140	90	
	45	156	94	60	

For kinetic limited pollutants, the temperature effects on the mass transfer can be negligible. Therefore, the biodegradation rate and the BF performance are improved by raising the temperature up to an optimum value [18]. Cox et al. (2001) [95] studied the performance of a BTF for ethanol vapors elimination at 53 °C and 22 °C. They observed a higher degree of ethanol mineralization of 60% at 53 ˚C comparing with 46% at 22 ˚C. The BF RE were the same for

both temperatures as 60% for an IL of 230 g m^{-3} h^{-1}. However, increasing temperature above 64 °C hampered the performance [95]. Lim et al. (2006) [91] demonstrated an optimum BF temperature for ethanol removal as 30 °C (RE of 82% for IL of 170 g m^{-3} h^{-1}). Feizi et al. (2016) [96] evaluated an n-butanol BF under different temperatures ranging from 30 to 45 °C. They obtained the highest RE of 85% for an IL of 156 g m^{-3} h^{-1} at 35 °C. For acetone biofiltration in the range of 30-45 °C, the optimum temperature for microbial growth rate and biodegradation rate was reported to be 40 °C for acetone inlet concentrations ranging from 0.1 to 0.7 g m^{-3} [97]. Therefore, mass transfer limited pollutants removal in BFs and BTFs could be limited by temperature effects on mass transfer and thermodynamic equilibriums. However, for kinetic limited pollutants, increasing temperature (up to an optimum value) can have a favorable effect on pollutant biodegradation.

2.6.4 Empty bed residence time (EBRT)

Elevating EBRT in BFs can improve the performance and ECs of mass transfer limited pollutants [18] since the pollutant exposure time to the biofilm phase is long enough and a gas-biofilm phase pseudo equilibrium can be established [89]. Vergara-Fernández et al. (2012) [89] obtained a doubled EC of 36 g m^{-3} h^{-1} comparing with an EC of 17 g m^{-3} h^{-1} when the EBRT increased almost two fold from 2 to 3.7 min for a constant n-pentane IL of 50 g m^{-3} h^{-1} in a BF. Rene et al. (2009) [98] varied the EBRT from 2 min to 20 s in a styrene BF. For a complete removal (RE=100%), they obtained a higher EC of 260 g m^{-3} h^{-1} at the longer EBRT (2 min) comparing to an EC of 200 g m^{-3} h^{-1} at the shorter EBRT of 20s (styrene inlet concentration = 5 g m^{-3}). For CH_4 BFs, the EBRT should be longer than 4 minutes [29, 32, 67, 99-104]. Nikiema and Heitz (2009) [104] evaluated the effect of gas flow rate (0.06 - 0.3 m^3 h^{-1}) on CH_4 bioconversion in a BF for an inlet concentration of 1.5 g m^{-3}. When the EBRT decreased from 17.5 to 3.2 min, the RE decreased from 100 to 40%.

Therefore, the EBRT for mass transfer limited BFs should be higher than 90 s or even higher than 4 min for CH_4. Rajamohan et al. (2015) [41] obtained a complete degradation of styrene for an IL of 80 g m^{-3} h^{-1} at an EBRT of 118 s.

On the other hand, for kinetic limited pollutants, long EBRTs higher than 3 min could have a dramatic effect on the BF performance [14]. In this regard, a great amount of the pollutant is eliminated and produces excess biomass just at the bottom section of an upflow BF [85, 105]

and causes excess pressure drop [14, 106]. Therefore, for kinetic limited components like alcohols, EBRTs are usually less than 1 min [107]. For instance, Palomo-Briones et al. (2015) [108] reported an EBRT of 60 s as an optimum value for methanol biofiltration (IL of 330 to 800 g m^{-3} h^{-1}).

2.6.5 Microorganisms

The microorganisms are key parameters on biodegradation in biofiltration [7]. Filamentous fungus with large surface area and hyphaes facilitate the removal of mass transfer limited pollutants and uptake them faster than bacteria into the biofilm [11, 16]. Nevertheless, inherent excess growth of filamentous fungi may cause problems like channeling, clogging and high pressure drop [16]. In addition, usually their slow growth comparing to bacteria makes a longer startup time as a requirement [109]. Nevertheless, the coexistence of fungi and methanotrophic bacteria in a CH_4 BF resulted to an RE of 90% and an EC of 39 g m^{-3} h^{-1} for an IL of 43 g m^{-3} h^{-1} [110] which supported an enhanced BF performance comparing with bacteria-based CH_4 BFs [111, 112]. Garcia-Pena et al. (2001) [113] obtained an EC_{max} of 361 g m^{-3} h^{-1} for an IL of 400 g m^{-3} h^{-1} for toluene biodegradation in a BF inoculated with fungi (*Scedosporium apiospermum* TB1), 6 times greater than the EC obtained for a bacterial BF. For n-hexane biodegradation in a fungal BF, an average EC of 60 g m^{-3} h^{-1} (IL= 120 g m^{-3} h^{-1}) was twice higher comparing with a bacterial-based BF [114] under the same operating conditions. The comparison of xylene biofiltration with fungal (*Phanerochaete chrysosporium* and *Cladosporium sphaerospermum*) and bacterial consortium (*EVB110*) was conducted by Jorio et al. (2009) [115]. For ILs lower than 50 g m^{-3} h^{-1}, no difference was observed between the two BFs in terms of EC. However, the fungi BF withstood better at ILs exceeding 50 g m^{-3} h^{-1}.

Fungi BFs have been reported to maintain their microbial activity under transient conditions such as shock loads or shutdowns [116]. Rene et al. (2009) [98] applied a styrene shock load from 50 to 500 g m^{-3} h^{-1} (gas flow rate of 0.15 m^3 h^{-1}) for 7 h and observed a RE reduction from 70 to 30%. They also applied a 7-day shutdown of styrene and nutrient simultaneously and observed a 10% decrease in terms of styrene RE. However, the responses of the BF after the shock load and the shutdown in terms of biocatalysts re-acclimation were immediate. A similar conclusion was attained in terms of immediate recovery when a fungi BTF, inoculated with *Sporothrix variecibatus*, was subjected to an styrene shock load from 800 to 2000 g m^{-3} h^{-1} [117].

Therefore, fungi or a mixture of fungi and bacteria is suggested as an inoculation for mass transfer limited pollutants removal (CH_4, n-hexane, xylene) in BFs. The microbial culture for kinetic limited pollutants removal like alcohols in BFs were usually provided by mixed cultures [118, 119], a leachate from another biofilter [53] or even no inoculation [120].

2.7 Biofiltration of mass transfer and kinetic limited pollutants in a mixture

Many industries may produce mass transfer and kinetic limited pollutants simultaneously. Therefore, BFs should be capable of eliminating a mixture of the pollutants. Although the detailed behavior of mixtures in BFs in the case of kinetic and mass transfer is still limited, some attempts have been done to report the interactions effects between components in a mixture of pollutant vapors. Dixit et al. (2012) [57] pointed out the positive effect of low ILs of n-propanol (<50 g m^{-3} h^{-1}) as a kinetic limited pollutant on toluene as a mass transfer limited pollutant degradation in a compost–wood chips based BF possibly due to a more enhance biomass growth. In contrast, for high ILs of n-propanol (>50 g m^{-3} h^{-1}), they observed a negative effect on the toluene BF performance most probably due to a kinetic competition between styrene and n-propanol. However, n-propanol elimination was not influenced by toluene concentration variations (0-2.64 g m^{-3}) in the BF. Paca et al. (2007) [121] examined the interactions effects in a BTF for a mixture of mass transfer limited (toluene, xylene) and kinetic limited (MEK, methyl isobutyl ketone and n-butyl acetate) compounds. Increasing the IL of mass transfer limited pollutants from 6 to 16 g m^{-3} h^{-1} dropped their REs from 90 to 60 % with no significant influence on RE of the kinetic limited components (ILs variation from 5 to 14 g m^{-3} h^{-1}). Nevertheless, increasing the IL of kinetic limited components from 5 to 14 g m^{-3} h^{-1}, decreased the RE of mass transfer limited components from 90 to 55% (ILs variation from 6 to 16 g m^{-3} h^{-1}) with a slight reduction (4%) for kinetic limited components RE. A similar conclusion was obtained in the biofiltration of a mixture of α-pinene (mass transfer limited) and methanol (kinetic limited) [122]. The presence of methanol at IL of 145 g m^{-3} h^{-1} decreased the α-pinene RE from 100 to 75% for an α-pinene IL in the range of 19 to 45 g m^{-3} h^{-1}. However, α-pinene had no significant effect on the methanol degradation. Paca et al. (2012) [123] evaluated the co-treatment of styrene (mass transfer limited) and acetone (kinetic limited) in a BF and a BTF when the styrene IL was fixed at 3 g m^{-3} h^{-1} and the acetone IL varied from 3 to 55 g m^{-3} h^{-1}. Up to an acetone IL of 25 g m^{-3} h^{-1}, both pollutants were completely removed. However, when the acetone IL

exceeded 25 g m^{-3} h^{-1}, the styrene REs declined to 90 and 80% in the BF and the BTF respectively. This reduction was addressed to easy bioavailability and biodegradability of acetone in comparison with styrene.

Therefore, in a mixture, the mass transfer limited pollutant removal could be more affected by the kinetic limited pollutant concentration since kinetic limited pollutants like alcohols are favorably soluble and biodegradable [122]. In a mixture of hydrophobic (mass transfer limited) and hydrophilic (kinetic limited) vapors removal in a BF, if the hydrophobic component is soluble in the hydrophilic component, the enhanced solubility of the hydrophilic compound may increase the bioavailability of the hydrophobic pollutant for the biocatalysts [124, 125]. In this regard, Hassan and Sorial (2010) [124] demonstrated that the presence of benzene (benzene IL variations from 20 to 60 g m^{-3} h^{-1}) in a mixture with n-hexane (2:1 and 3:1 $v_{benzene}/v_{hexane}$) could improve the n-hexane removal (n-hexane IL variations from 5 to 20 g m^{-3} h^{-1}). Benzene removal was almost complete for benzene ILs lower than 30 g m^{-3} h^{-1} due to the high affinity of benzene to the biofilm. However, n-hexane removal was not higher than 75% for the same range of IL (hexane ILs <30 g m^{-3} h^{-1}). The results showed a poorer performance comparing to an identical BF for only n-hexane removal with an average RE of 82% (hexane IL of 6 g m^{-3} h^{-1}) [126].

In a BF for simultaneous elimination of mass transfer and kinetic limited pollutants, individual sudden IL variations for each type of pollutant might end up to transient conditions. A sudden increase of methanol (kinetic limited pollutant) IL from 50 to 600 g m^{-3} h^{-1} dropped an α-pinene RE from 40 to 5% for a constant α-pinene IL of 25 g m^{-3} h^{-1} in a BTF with no significant change for methanol RE (RE>90%) [63]. In contrast, an α-pinene shock load from 25 to 415 g m^{-3} h^{-1} under a constant methanol IL of 100 g m^{-3} h^{-1}, suddenly dropped the α-pinene RE from 25 to 15% with no influence on methanol RE (RE> 90%). It can be concluded, for a mixture of mass transfer and kinetic limited pollutants in BFs, the mass transfer limited pollutant is more affected either by its shock load or by a shock load of the kinetic limited pollutant. However, a shock load of mass transfer limited pollutant usually reduces its RE with no significant effect on the kinetic limited pollutant elimination.

2.8 Innovative configuration of BFs to overcome mass transfer and kinetic limitations

2.8.1 Two liquid phase biotrickling filter (TLP-BTF)

Addition of a non-aqueous liquid phase (NALP) like silicone oil or hexadecane to a BTF may improve the performance either for mass transfer or kinetic limited pollutants [21, 127-129]. Organic phase selection and organic to aqueous phase optimum volume ratio are the two most important parameters which should be taken into account for using a second absorbent liquid phase in a BTF [127]. NALPs should be immiscible in water, non-toxic, non-biodegradable, inexpensive and non-destructive for packing materials [21, 127]. A number of studies suggested silicone oil as an NALP candidate which satisfied to some extend all the requirements [21, 130]. The optimum volume ratio of organic phase to water phase was reported as 10-20% (v/v) [21, 130]. Relatively low viscosity, non-toxicity for microorganisms and high affinity for mass transfer limited pollutants are some properties of silicone oil which make it suitable as a second phase [21, 127, 130].

Two liquid phase biotrickling filters were mostly used to overcome mass transfer limitations. Biotrickling filters with an NALP phase (silicone oil) showed a better performance for CH_4 abatement comparing to regular BTFs [28, 131]. Table 2.6 presents some studies on BTFs for mass transfer limited pollutants abatement. Rocha-Rios et al. (2009) [28] obtained higher CH_4 EC of 60 g m^{-3} h^{-1} (IL=130 g m^{-3} h^{-1}) in a TLP-BTF with 10% (v/v) silicone oil as an NALP compared to an EC of 25 g m^{-3} h^{-1} for the same IL in a BTF. Lebrero et al. (2015) [131] obtained an EC of 45 g m^{-3} h^{-1} for an IL of 250 g m^{-3} h^{-1} for an EBRT of 4 minutes in a CH_4 TLP-BTF (25% v/v silicone oil) with a corresponding RE of 18%. The RE of the CH_4 TLP-BTF was in the range of the studies conducted by Rocha-Rios et al. (2009) [28] and Avalos Ramirez et al. (2012) [29] for BTFs for identical EBRTs of 4 min. However, the CH_4 EC was 2 fold higher in the TLP-BTF comparing to the BTFs [131]. The improvement of the CH_4 REs and ECs in TLP-BTFs might be attributed to absorption properties of silicone oil for CH_4 which provided a higher rate of CH_4 mass transfer from gas to the biofilm phase [21].

Table 2.6: Effect of NALPs on mass transfer limited pollutant's removal in TLP-BTFs

Pollutant	Bioreactor	NALP	IL ($g\ m^{-3}\ h^{-1}$)	EC ($g\ m^{-3}\ h^{-1}$)	RE (%)	References
CH_4	BTF	-	160	25	16	[28]
	TLP-BTF	Silicone oil (10% v/v)	130	60	46	
CH_4	TLP-BTF	Silicone oil (25% v/v)	250	45	18	[131]
n-hexane	BTF	-	170	85	50	[132]
	TLP-BTF	Silicone oil (10% v/v)	170	153	90	
Styrene	BTF	-	110	70	64	[133]
	TLP-BTF	Silicone oil (5% v/v)	110	110	100	
α-pinene	BTF	-	880	330	38	[134]
	TLP-BTF	Silicone oil (5% v/v)	1920	1890	98	

For n-hexane removal in a BTF, addition of 10% (v/v) silicone oil enhanced the pollutant mass transfer into the biofilm phase and increased the RE from 50 to 90% for an average IL of 170 $g\ m^{-3}\ h^{-1}$ [132]. Montes et al. (2010) [134] reached an EC of 1890 $g\ m^{-3}\ h^{-1}$ for an α-pinene IL of 1920 $g\ m^{-3}\ h^{-1}$ in the presence of 5% (v/v) silicone oil comparing with a BTF with an EC of 330 $g\ m^{-3}\ h^{-1}$ for an IL of 880 $g\ m^{-3}\ h^{-1}$. Despite the mass transfer enhancement properties, there were some other advantages for TLP-BTFs. Zamir et al. (2015) [133] obtained EC_{max}s of 110 and 70 $g\ m^{-3}\ h^{-1}$ in a TLP-BTF (5% (v/v) silicone oil) and BTF respectively for a styrene IL of 110

g m^{-3} h^{-1}. In addition, they found the TLP-BTF to be less temperature dependent compared with the BTF. When the temperature increased from 35 to 40 °C, no significant change of RE of 90% was observed in the TLP-BTF. However, temperature variation from 35 to 40 °C resulted in a RE decline from 90 to 70% in the BTF. Rene et al. (2011) [117] reported a TLP-BTF to be more tolerant to 8 hours styrene shock load. In the TLP-BTF with 10% (v/v) silicone oil, sudden variation of IL from 100 to 800 g m^{-3} h^{-1} decreased the RE from 100 to 80 %. However, applying lower styrene shock load from 100 to 400 g m^{-3} h^{-1} in a BTF (without silicone oil) significantly dropped the RE from 60 to 25%.

Two liquid phase biotrickling filters are usually used to overcome mass transfer limitations. Nevertheless, they might be used for kinetic limited pollutants like alcohols with potential of toxicity for the biocatalyst. In this case, the NALP absorbs the pollutant instantly and releases it gradually to reduce the excess availability of the pollutant in the biofilm phase [127].

2.8.2 Innovative feeding strategies

In order to have a more homogenous distribution of biomass in BFs and BTFs, one solution is to split the inlet gas stream at 2 or 3 sections along the BF or BTF. In support of this fact, Mendoza et al. (2003) [135] divided a down-flow gas stream of a toluene polluted air into two equal gas streams (0.075 m^3 h^{-1} of each) and introduced them at two different inlet ports of a BTF. Due to more homogenous distribution of biomass, a RE of 80% for inlet concentrations over 2.5 g m^{-3} showed an improvement compared to a similar single feeding BTF with a maximum RE of 80% for inlet concentration of 0.8 g m^{-3}. Estrada et al. (2013) [136] compared a regular BF (EBRT=60 s) with a novel BF in which the polluted air stream (gas flow rate of 8.6 L min^{-1}) was split and introduced at three locations along the BF in order to obtain EBRTs of 60, 40 and 20 s for bottom, middle and top sections of the BF respectively. The target pollutant and the packing material were toluene and compost, respectively. The improved feeding method led to an EC of 80 g m^{-3} h^{-1} compared to 120 g m^{-3} h^{-1} for an IL of 150 g m^{-3} h^{-1} in the standard BF, due to lower gas turbulence (lower mass transfer coefficient) and shorter EBRT (60, 40 and 20 s per section) in the split feeding BF. However, by using the split feeding method, pressure drop never exceeded 25 mmH_2O m^{-1}_{bed} due to more uniform distribution of biomass while in the standard BF, the maximum pressure drop reached 400 mmH_2O m^{-1}_{bed} (IL=150 g m^{-3} h^{-1}). Therefore, split feeding could be suggested for kinetic limited pollutants with high potential of

biomass production and not for mass transfer limited pollutants. For mass transfer limited pollutants, recycling a ratio of outlet gas stream to the earlier sections of BTFs may allow a higher EBRT in the BTF. Estrada et al. (2014) [27] added a recycling gas stream with a flow rate of 18 L min^{-1} from the top to the bottom of a CH_4 BTF. Using this method enhanced the CH_4 mass transfer. The EC increased two folds from 15 to 30 g m^{-3} h^{-1} for an IL of 230 g m^{-3} h^{-1}.

2.8.3 Two-stages and hybrid BFs

Two BFs in series or a combination of two BFs in one column (hybrid BFs) can be helpful when a mixture of mass transfer and kinetic limited pollutant is present [137]. It is beneficial to use one bioreactor for kinetic limited pollutants and the other for mass transfer limited pollutants. Table 2.7 presents some examples of hybrid BFs for mass transfer and kinetic limited pollutants elimination.

Table 2.7: Removal of mass transfer and kinetic limited pollutants in hybrid biofilters

Pollutant	Hybrid bioreactor	IL (g m^{-3} h^{-1})	EC (g m^{-3} h^{-1})	RE (%)	References
n-hexane	BF+BF	300	210	70	[138]
p-xylene	BF+BF	85	80	95	[139]
α-pinene	BTF+BF	50	45	90	[140]
H_2S	BTF+BF	20	20	98	
Methanol	BTF+BF	200	200	98	
Benzene	Bubble column +BF	120-300	45-86	15-72	[141]

Rene et al. (2009) [140] fed a mixture of hydrogen sulfide (H_2S), methanol, and α-pinene as inorganic, kinetic limited and mass transfer limited components, respectively to a series of a BTF and a BF. Complete degradations (RE>98%) of H_2S and methanol occurred in the BTF for ILs of 20 and 200 g m^{-3} h^{-1}, respectively. However, less than 40% of α-pinene (IL of 50 g m^{-3} h^{-1}) was eliminated. Using a BF after the BTF supported a global EBRT of 2 min to ensure an α-

pinene RE higher than 90%. Wu et al. (2006) [139] also took the advantage of global EBRT of 2 min for the elimination of p-xylene as a single mass transfer limited pollutant in two BFs in series to obtain a maximum EC and RE of 80 g m^{-3} h^{-1} and 95%, respectively (IL=85 g m^{-3} h^{-1}). Spigno et al. (2003) [138] doubled the EC of 150 g m^{-3} h^{-1} of an n-hexane BF by connecting the BF to an identical BF for a total IL of 300 g m^{-3} h^{-1}. Removal efficiencies in the second BF (RE=70%) were higher than in the first BF (RE=50%) due to lower n-hexane inlet concentrations introduced to the second one. Yeom and Yoo (1999) [141] used a hybrid BF consisting of a bubble column and a regular BF for benzene removal. The RE varied in the range of 60 to 100% for corresponding IL variations from 120 to 300 g m^{-3} h^{-1}. This type of hybrid BF could be more flexible for inlet load fluctuations such that the bubble column could absorb the sudden variation of loading instantly and release it gradually for the BF [141].

2.9 Conclusion

Biofilters (BFs) and biotrickling filters (BTFs) have been used as promising techniques either for mass transfer limited or kinetic limited vapor organic pollutants abatement. Gaseous alkanes (CH_4), alkenes (C_2H_4), liquid alkanes (n-pentane and n-hexane), liquid alkenes like α-pinene and some aromatics (toluene, styrene and xylene) were discussed as mass transfer limited pollutants based on their water solubility, dimensionless Henry's law constant and vapor pressure. Due to the existence of a gas phase and a liquid-biofilm phase in contact to each other, pollutants with mass transfer limitations are less available in the biofilm phase which diminishes the performance parameters like RE and EC in BFs. On the other hand, almost no mass transfer limitations for kinetic limited pollutants like alcohols (methanol, ethanol and n-propanol), VFAs (acetic acid and butyric acid) and ketones (MEK and acetone) may end up to toxicity for biocatalysts, excess growth of biomass and pressure drop problems in BFs. According to the limitations of a target pollutant, some operating parameters like support media, water content of the filter bed, temperature, EBRT and microorganisms play an important role on the limitations and consequently on the BF performance. In addition, operating parameters may have a conflict of effect on a target pollutant removal in a BF. For instance, decreasing temperature or water content of the filter bed could improve the performance of a mass transfer limited pollutant unlike a kinetic limited pollutant in a BF. Therefore, for simultaneous biofiltration of a mass transfer and kinetic limited pollutants, it is important to set optimum operating conditions which are suitable both for the mass transfer limited and for the kinetic limited pollutants. Recently,

improved configurations of BFs and BTFs have been developed as two liquid phase biofilters (TLP-BTFs), two stages and hybrid BFs and BFs with modified feeding strategies like split feeding, to overcome mass transfer and kinetic limitations. The improved BFs have been successfully used for single and mixture of pollutants. However, the issue is still new and needs more attention and investigation.

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CHAPTER 3. Performance evaluation of a methane biofilter under steady state, transient state and starvation conditions

Avant propos:

L'article "Performance evaluation of a methane biofilter under steady state, transient state and starvation conditions*"* a été publié dans le Journal "*Water, Air, & Soil Pollution*" 227.6 (2016) 1-11.

TITRE: Évaluation de la performance d'un biofiltre traitant le méthane en régimes permanent et transitoire et en conditions de carence

Title: Performance evaluation of a methane biofilter under steady state, transient state and starvation conditions

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Contribution to the document: This paper is relevant to the first objective of the thesis. The performance of a CH_4 biofilter under steady state and transient state conditions (e.g., shock loads and starvations) was evaluated. The ability of the biofilter to deal with the harsh conditions and the biofilter recovery after the transient conditions were discussed.

Performance evaluation of a methane biofilter under steady state, transient state and starvation conditions

3.1 Résumé

Un biofiltre fonctionnant en régime permanent, en régime transitoire et sous des conditions de carence, ayant un garnissage de type inorganique a été utilisé pour éliminer le méthane (CH_4) présent dans un effluent gazeux. En régime pseudo-permanent, l'influence de la concentration du CH_4 à l'entrée du biofiltre dans une gamme variant entre 1000 et 13000 ppmv sur la performance du biofiltre a été étudiée. Le débit volumique d'air a été maintenu constant à 3 L min^{-1} ce qui correspond à un temps de résidence en fût vide (EBRT) de 6 min. La flexibilité du biofiltre sous des conditions transitoires a été évaluée selon 2 stratégies : la charge à l'entrée du CH_4 a varié entre 13 et 65 g m^{-3} h^{-1} par des variations effectuées sur la concentration de CH_4 de 2000 à 10000 ppmv ou par des variations du débit volumique de 3 à 15 L min^{-1}. Par la suite, l'influence des nutriments et de la privation de CH_4 ont été étudiée. Le biofiltre a montré une excellente performance pour de larges gammes de concentration de CH_4 allant de 1000 à 13000 ppmv. Pour une gamme de concentration de CH_4 variant entre 1000 et 4000 ppmv, la conversion du CH_4 était supérieure à 75 %. La capacité d'élimination maximale (CE) obtenue dans le cadre de cette étude a été de 45 g_{CH4} m^{-3} h^{-1} pour une charge à l'entrée de CH_4 de 87 g m^{-3} h^{-1}. Dans le cas de variations soudaines de charges à l'entrée (13 à 65 g m^{-3} h^{-1}) obtenues soit en modifiant la concentration de CH_4 soit en modifiant le débit volumique, la réponse du biofiltre était presque instantanée.

Mots clefs: Biofiltre, méthane, charge à l'entrée, charge transitoire, variations par à-coups, conditions de carence

3.2 Abstract

An inorganic based-bed biofilter was used to eliminate methane (CH_4) from an air stream under pseudo steady state, transient state (shock loads) and starvation conditions. Under pseudo steady state conditions, the effect of inlet CH_4 concentration in the range of 1000-13000 ppmv on the biofilter performance was studied. The air flow rate was kept constant at 3 L min^{-1}, corresponding to an empty bed residence time (EBRT) of 6 min. The flexibility of the biofilter

under transient conditions was evaluated by two strategies: Inlet loads (IL) varied from 13 to 65 g m^{-3} h^{-1} by changing inlet concentrations from 2000 to 10000 ppmv or by changing air flow rates varied from 3 to 15 L min^{-1}, separately. Finally, the effects of nutrients and CH_4 starvations were evaluated. The biofilter performance was promising for the treatment of a wide range of concentrations of off gas emissions polluted with CH_4 (1000-13000 ppmv). For CH_4 concentrations ranging from 1000 to 4000 ppmv, the removal efficiency (RE) remained higher than 75%. The maximum elimination capacity (EC) obtained in this study was 45 g m^{-3} h^{-1} for an IL of 87 g m^{-3} h^{-1}. In case of sudden variations of ILs (13 to 65 g m^{-3} h^{-1}) either by changing the inlet concentration or by modifying the flow rate, the responses of the biofilter were almost instantaneous.

Keywords: biofilter, methane, inlet load, transient loads, shock loads, starvation conditions

3.3 Introduction

Methane (CH_4) and carbon dioxide (CO_2) are the two most important pollutants causing global warming. The concentrations of CH_4 and CO_2 in the atmosphere are 1.7 and 380 ppmv, respectively (2012) [142, 143]. The global warming potential (GWP) of CH_4 is 25 times higher than CO_2 on a 100 year time horizon [142]. Since CH_4 emissions increasing rate (0.7 % increase annually worldwide) is two fold higher than CO_2 [28, 142], it is necessary to reduce the CH_4 emissions into the atmosphere [9]. Methane is emitted from natural and anthropogenic sources [144]. Nowadays, natural sources like wetlands and oceans contribute to 40% of total CH_4 emissions while anthropogenic activities like landfills, natural gas refineries, wastewater anaerobic treatment units and livestock generate more than 60% of total CH_4 emissions in the world [3] which amounts to an accumulation of 20 Mt CH_4 $year^{-1}$[145]. If the CH_4 concentration in industrial effluents is higher than 5% (v/v), chemical oxidation can be an appropriate process to remove CH_4. However, more than 50% of CH_4 emissions have concentrations lower than 3% (v/v) [146]. In those cases, a promising alternative is biofiltration. Biofiltration is based on the microbial transformation of CH_4 by methanotrophs, bacteria for CH_4 degradation, to end products such as CO_2, water and biomass [13, 147]. However, CH_4 biofiltration is limited by the CH_4 mass transfer from gas to biofilm phase and thermodynamic equilibrium (dimensionless Henry's law constant for CH_4 is 33.5 at 30 ˚C) [28, 128]. Inlet load (IL) is a key parameter for

CH_4 biofiltration. The majority of the investigations on CH_4 biofiltration applied EBRTs longer than 4 min to ensure the maximum mass transfer [32, 104]. However, performance evaluation of a CH_4 biofilter for a wide range of ILs (<10 to >100 g m^{-3} h^{-1}) has received little attention especially when the IL is achieved by changing CH_4 inlet concentration. On the other hand, a sudden variation of air flow rate or polluted gas inlet concentration, as well as an absence of the pollutant for a period of time, is common due to the inherent nature of many industries [148]. Biofilters are supposed to be flexible enough to various changes of inlet load patterns including shock loads or starvation of nutrients or substrates [9]. Most of the investigations on biofilters were done under pseudo steady state conditions and the dynamic behavior of biofilters can be found only in a few studies [105, 149]. According to our best knowledge, no study has examined the effect of shock loads or starvation on CH_4 biofiltration.

The aim of this study was to evaluate the performance of a laboratory scale biofilter for CH_4 elimination at different inlet load patterns: normal load, shock load and CH_4 and nutrient starvations. The effects of CH_4 inlet concentration on the biofilter performance were studied during normal loading conditions. In addition, the EC_{max} (maximum capacity of a biofilter to eliminate a typical pollutant) [94] was obtained. The transient behaviors of the biofilter during shock loads were then examined in order to evaluate the flexibility of the biofilter. In addition, the biofilter responses after starvation of nutrient solution as well as both of substrate and nutrient solution were evaluated.

3.4 Materials and methods

3.4.1 Experimental set-up

Figure 3.1 shows the schematic of the biofilter. The biofilter (made of Plexiglas) consisted of three identical stages. Each stage had a diameter of 150 mm and a height of 330 mm. The total volume of the biofilter was about 18 L. A stone material with a void fraction of 0.43 was used as a support media. Gallastegui et al. (2011) [150] explained some characteristics of the packing. A humid air stream was mixed with pure CH_4 (Praxair Inc., Canada) and introduced at the bottom of the biofilter. The air and CH_4 flow rates were adjusted by flow controllers (Brooks, Series 0154 and 0254, USA).

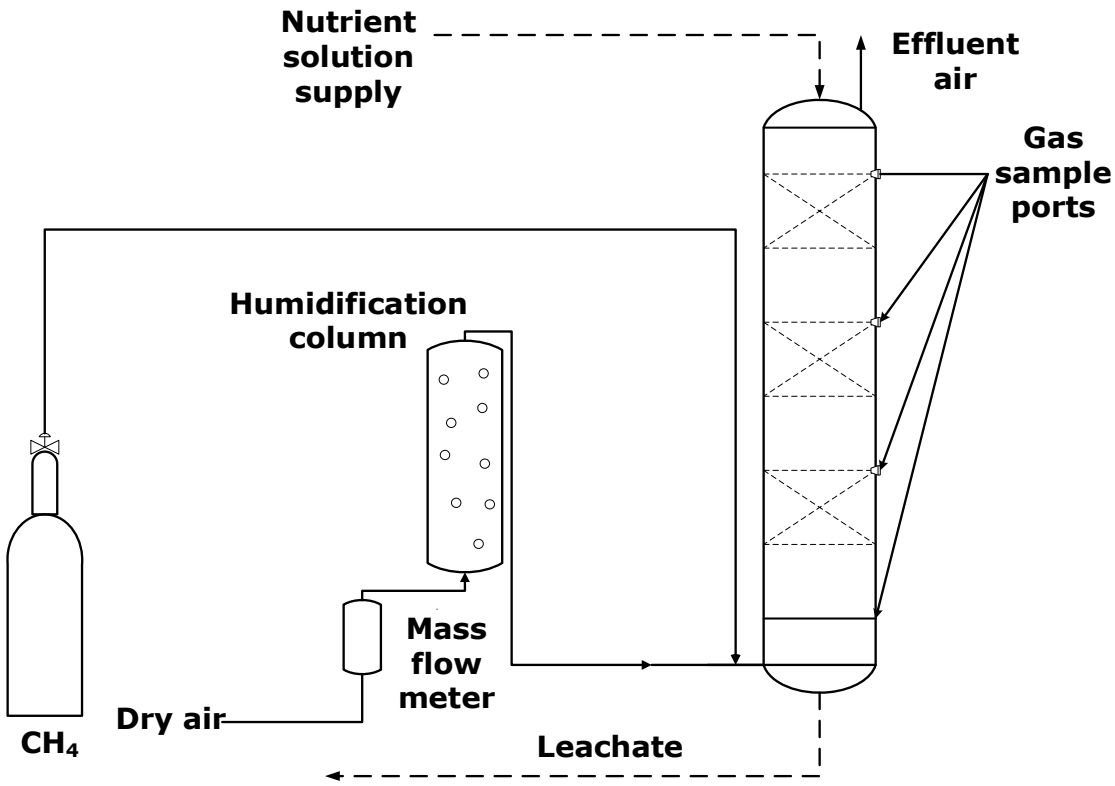

Figure 3.1: Experimental set up of the biofilter

3.4.2 Microbial culture and inoculation

One liter of activated sludge (Sherbrooke wastewater treatment plant) was prepared to inoculate the biofilter. Before inoculation, the filter bed was washed with tap water. Then, 1.5 L of nutrient solution was fed to the biofilter to provide sufficient nutrients for the inoculum. Finally, the one liter activated sludge was introduced at the top of the biofilter which was already supplied with CH_4 and humid air. The leachate was collected and recycled several times to the biofilter to make sure that each section was exposed to the solution. In order to accelerate the microbial growth and to ensure a uniform distribution of microbial culture in the biofilter, the sludge solution was recycled for 7 days.

3.4.3 Nutrient solution

The nutrient solution was fed to the biofilter at a rate of 1.5 L min^{-1} (for 1 min) once a day. The composition and concentrations of the nutrient solution in terms of nitrogen and phosphorus were the same used by Ménard et al. (2012) [151].

3.4.4 Analytical methods

Gas samples (CH_4 and CO_2) were collected from four sampling ports along the bed height. Three ports were located at the top of each section while one port was used to measure the inlet CH_4 concentration. Methane concentration was measured by a total hydrocarbon analyzer (FIA 510 Horiba, USA). In addition, a CO_2 gas analyzer (VIA 510) was used to determine CO_2 concentrations from gas sample ports.

3.4.5 Biofilter operating parameters

The biofilter performance was evaluated using the following parameters:

Elimination capacity $(EC) = \frac{(C_{Gi} - C_{Go}).Q}{V_f}$ [g m^{-3} h^{-1}]

Removal efficiency $(RE) = \frac{(C_{Gi} - C_{Go})}{C_{Gi}} \times 100$ [%]

Inlet load $(IL) = \frac{Q \times C_{Gi}}{V_f}$ [g m^{-3} h^{-1}]

CO_2 production rate $(PCO_2) = \frac{(CO_{2_{out}} - CO_{2_{in}}).Q}{V_f}$ [g m^{-3} h^{-1}]

Where C_{Gi} and C_{Go} are the inlet and outlet CH_4 concentrations [g m^{-3}] respectively and $CO_{2_{in}}$ and $CO_{2_{out}}$ are the inlet and outlet CO_2 concentrations respectively. Q is the gas flow rate [m^3 h^{-1}] and V_f [m^3] is the volume of the biofilter.

3.4.6 Experimental method

The study was separated into three phases based on pseudo steady state, transient state IL and starvation patterns.

3.4.6.1 Pseudo steady state IL patterns

Pseudo steady state experiments were performed at ten levels of CH_4 inlet concentration in the range from 1000 to 13000 ppmv (1 ppmv (CH_4) = 0.00066 g (CH_4) m^{-3}). A wide range of CH_4 inlet concentrations was selected in order to obtain the maximum performance of the biofilter in terms of EC and RE as well as the CH_4 inlet concentration at which the performance of the biofilter began to decrease. This range of inlet concentration corresponds to the CH_4 IL range from 7 to 87 g m^{-3} h^{-1}. Gas flow rate was kept constant at 3 L min^{-1}, which corresponds to an EBRT of 6 min. Daily measurements for several days were performed until the biofilter reached pseudo steady state conditions (±5% variation of the EC, RE and CO_2 production rate on average) and the corresponding RE, EC and CO_2 production rate were calculated.

3.4.6.2 Transient state IL patterns.

In the second phase, the performance of the biofilter under dynamic loading patterns was studied by applying two types of CH_4 inlet shock loads to the biofilter. Sudden variations of IL from 13 to 65 g m^{-3} h^{-1} (5 times its original value) were applied to the biofilter by two different methods. For the 1st method, the shock load was undertaken by a sudden variation of inlet concentration from 2000 to 10000 ppmv for a period of 5 days and then the inlet concentration was restored to its original value (2000 ppmv). For the 2nd method, a sudden variation of contaminated air flow rate from 3 to 15 L min^{-1} was applied for 7 days and then the flow rate brought back to 3 L min^{-1}.

3.4.6.3 Starvation

Starvations were applied to the biofilter in three steps in order to determine if the biofilter could tolerate the lack of both nutrient and CH_4 simultaneously. In step 1, the biofilter was fed with a CH_4 inlet concentration of 2000 ppmv, and a humid air flow rate of 3 L min^{-1} without any nutrient solution for 14 days. For the next 14 days, only tap water was added at a rate of 1.5 L min^{-1} (for 1 min each day) to the biofilter (step 2). In this step, CH_4 and humid air were still flowing through the biofilter. Then, in step 3, nutrient solution and CH_4 streams were removed from the biofilter for the next 30 days. Finally, nutrient solution addition and CH_4 feeding, at a flow rate of 3 L min^{-1} and an inlet concentration of 2000 ppmv, were restarted.

3.5 Results and discussion

3.5.1 Performance during pseudo steady state conditions

Figure 3.2 shows the influence of CH_4 inlet concentration on the biofilter performance. According to Figure 3.2, increasing the inlet concentration from 1000 to 13000 ppmv gradually decreased the biofilter performance from 87 to 52%. When CH_4 inlet concentration was increased from 1000 to 1300 ppmv, the RE decreased from 87 to 78%. The maximum RE (87%) was obtained at the lowest level of CH_4 inlet concentration of 1000 ppmv. Melse and Van Der Werf (2005) [112] could also achieve a maximum RE of 85% for the lowest CH_4 inlet concentration of 700 ppmv and an EBRT of 7 min. However, when the CH_4 inlet concentration was increased to 7500 ppmv, the biofilter's decreasing performance behavior was similar to the present study such that the RE diminished to 40% [112]. The decreasing trend of RE from 87 to 52% in the present study could be attributed to some CH_4 reaction limitations. Although, CH_4 solubility in water phase is poor, increasing the CH_4 inlet concentration would gradually increase the CH_4 concentration in the biofilm phase and might cause reaction limitations [104]. According to Figure 3.2, the RE decreasing trend was different in each range of the inlet concentration variation. During the inlet concentration increasing from 1300 to 4000 ppmv, the RE remained relatively constant around 77 % (±1.5). However, when CH_4 inlet concentration was increased from 4000 to 13000 ppmv, a reduction of RE from 75 to 52% was observed. Nikiema and Heitz (2009) [104] reported the inlet concentration to be a less significant factor on a CH_4 biofilter performance comparing to other parameters like gas flow rate. Therefore, the effect of CH_4 inlet concentration on the biofilter performance could be more significant if the CH_4 inlet concentration variation range is wide.

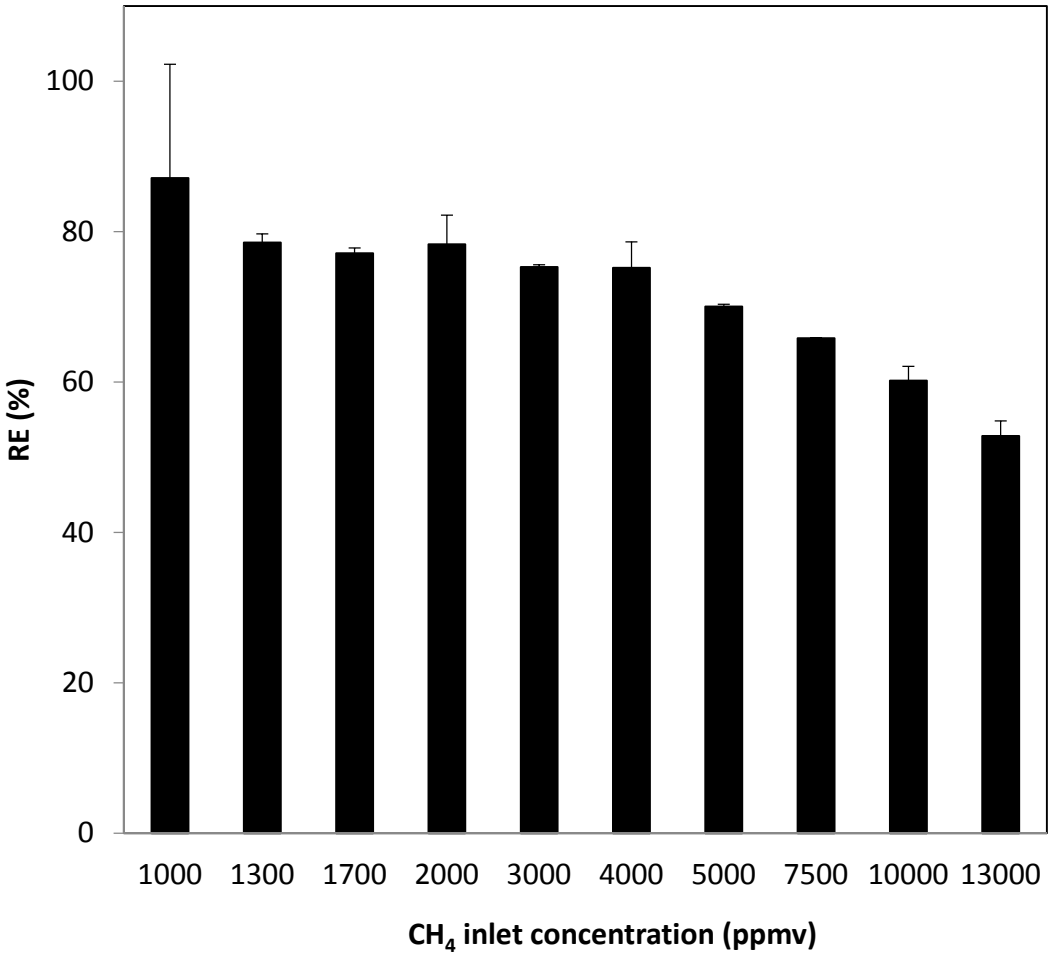

Figure 3.2: The biofilter performance as a function of CH_4 inlet concentration

Figure 3.3 shows EC as a function of ILs with values ranging from 7 to 87 g m^{-3} h^{-1} (CH_4 inlet concentrations from 1000 to 13000 ppmv and gas flow rate of 3 L min^{-1}). According to Figure 3.3, the maximum EC of the biofilter (EC_{max}), was obtained as 45 g m^{-3} h^{-1} for an IL of 87 g m^{-3} h^{-1} with the corresponding RE of 52%. For ILs lower than 25 g m^{-3} h^{-1}, the trend of EC as a function of IL was linear with a slight deviation from 100% RE line (theoretical). However, for higher values of ILs up to 87 g m^{-3} h^{-1}, a more significant deviation of 100% RE line (theoretical) was observed. Therefore, it can be pointed out that, in the present study, exceeding the inlet concentration of CH_4 of 4000 ppmv at an EBRT of 6 min (IL > 25 g m^{-3} h^{-1}) increased the EC with a significant reduction of RE (from 75 to 52%).

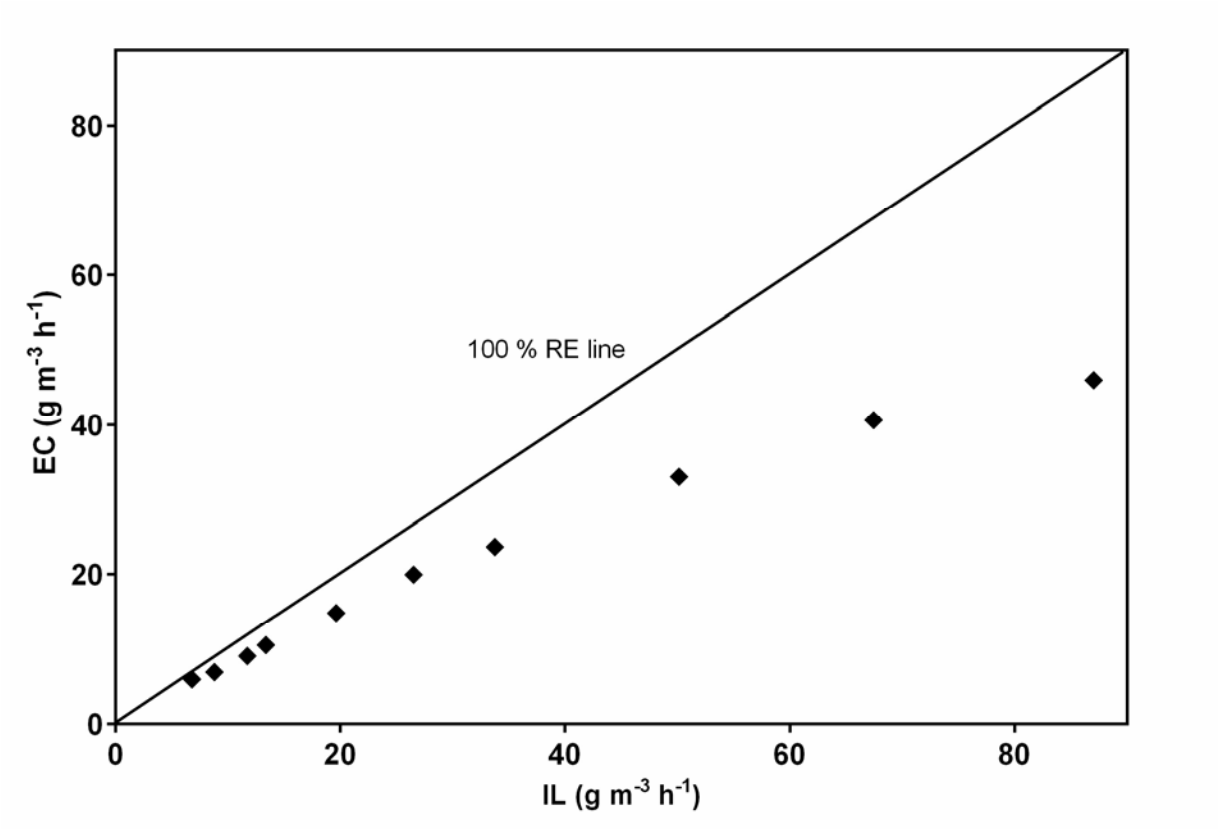

Figure 3.3: Elimination capacity as a function of CH_4 inlet load

Limbri et al. (2014) [33] studied a CH_4 biofilter performance by increasing IL from 15 to 70 g m^{-3} h^{-1} for an EBRT of 1.5 min. Similar to the present study, they observed a reduction of RE from 30 to 20% and an improvement in EC from 5 to 20 g m^{-3} h^{-1} for an EBRT of 1.5 min [33]. Relatively low values of EC (< 50 g m^{-3} h^{-1}) were mostly related to the poor solubility of CH_4 in the biofilm phase which reduced the bioavailability of CH_4 for microorganisms [128]. However, the EC_{max} of 45 g m^{-3} h^{-1} in the present study is comparable to other studies [28, 29, 32, 102]. The long EBRT could provide a sufficient contact time between CH_4 and the biofilm and produces an enhanced CH_4 mass transfer from gas phase to the biofilm phase [15]. In addition, the packing material provided a relatively high specific surface area (470 m^2/m^3) [150] which also ensured appropriate mass transfer of CH_4 from gas phase to the biofilm phase [18]. In order to have a better understanding about the contribution of biological reactions in the bioelimination of a pollutant, CO_2 production rate is helpful. In the case of complete mineralization of CH_4 without any biomass production, the stoichiometric theoretical mass ratio

PCO_2/EC is 2.75. Figure 3.4 shows the CO_2 production rate as a function of EC. When the ECs increased from 10 to 45 g m^{-3} h^{-1} (ILs from 13 to 87 g m^{-3} h^{-1}), the PCO_2/EC ratio increased from 1.8 to 2.4.

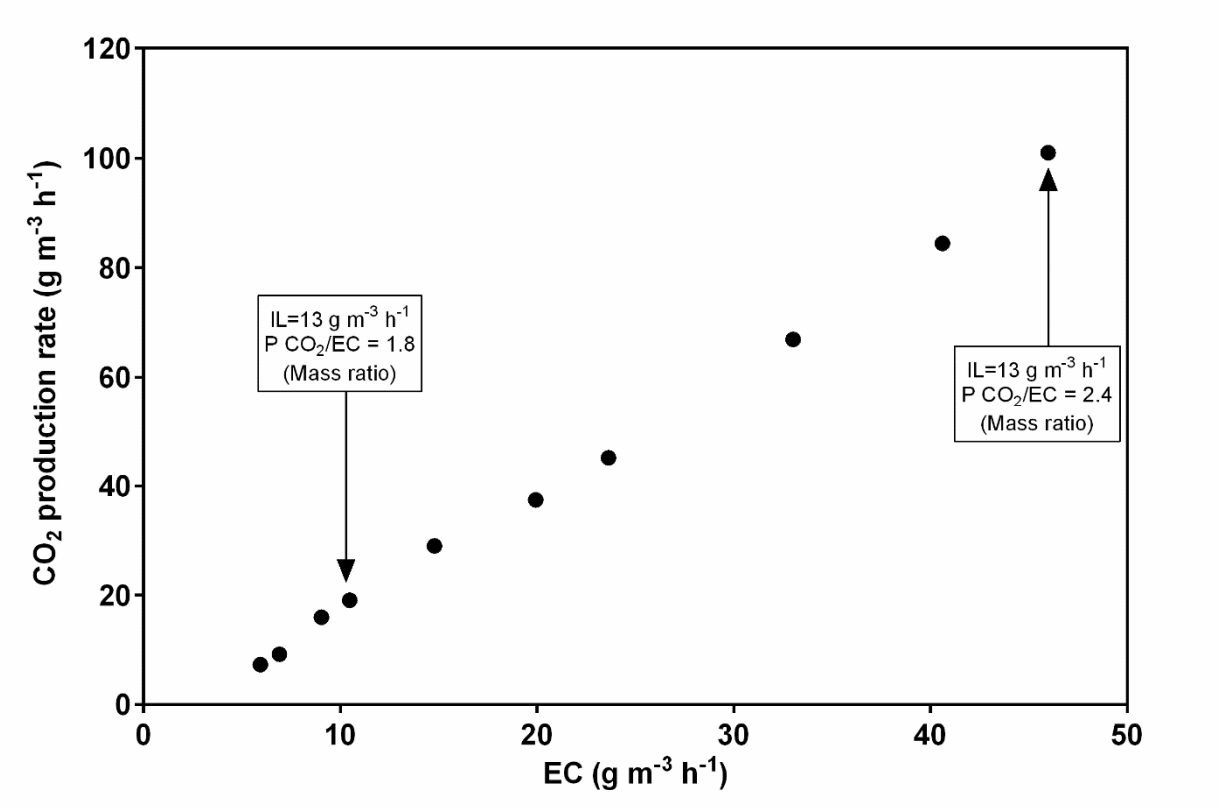

Figure 3.4: Carbon dioxide production rate as a function of CH_4 elimination capacity

In other words, the contribution of CO_2 in end products increased when the IL was increased. This shows that by increasing the CH_4 inlet concentration, the methanotrophs tended to produce more CO_2 as opposed to biomass for a constant IL [32].

3.5.2 Biofilter performance at unsteady state load patterns

3.5.2.1 Effect of shock load strategies

Figure 3.5a shows the behavior of the biofilter when a sudden variation of CH_4 inlet concentration from 2000 to 10000 ppmv, was applied (days 288-292) corresponding to an IL variation from 13 to 65 g m^{-3} h^{-1}. The gas flow rate was kept constant at 3 L min^{-1} (EBRT of 6 min). The sudden increase of IL resulted in a sudden increase of EC from 9 to 43 g m^{-3} h^{-1} with

no significant change of RE. The improvement of EC with a slight reduction of RE during the shock load showed that the biofilter could reliably treat CH_4 inlet concentrations higher than 2000 ppmv at an EBRT of 6 min even if the increase of the inlet concentration was quick. Park et al. (2009) [67] used a wider range of CH_4 inlet concentration variations in a biofilter. They performed step load increases for CH_4 such that the IL was increased and kept at a fixed value but it was not brought back to its initial value. They observed a significant reduction of RE from 99 to 59 % by varying the CH_4 inlet concentration from 5 to 10 % (v/v) (EBRT of 8 min). In addition, during 8 days with a CH_4 inlet concentration at 10 % (v/v), the RE remained unchanged at 59%. In the present study, during days 288 to 292, the EC and RE declined gradually from 43 to 38 g m^{-3} h^{-1} and from 65 to 55%, respectively. The RE reduction could be attributed to excess biomass production and some reaction limitations. Kim et al. (2014) [152] mentioned that the excess biomass production had a dramatic effect on the microbial community in a CH_4 biofilter. Figure 3.5b shows the CO_2 production rate due to the inlet concentration shock load. Injecting 5 times the original IL led to almost a 4 fold increase in CO_2 production rate from 20 to 72 g m^{-3} h^{-1}. This indicated that the biofilter microbial culture was able to tolerate shock loads by CH_4 inlet concentration variations.

Figure 3.6a shows the performance of the biofilter under the same sudden variation of IL from 13 to 65 g m^{-3} h^{-1} by changing the gas flow rate instead of the CH_4 inlet concentration. In other words, the inlet concentration was kept constant at 2000 ppmv and the flow rate increased suddenly from 3 to 15 L min^{-1} (an EBRT variation from 6 to 1 min). The RE, for a CH_4 inlet concentration of 2000 ppmv and an EBRT of 6 min, was in the range of 50-70% just before the shock load (days 250 to 267). On day 268 (the 1st day of the shock load), the RE declined to 15%. During the shock load, the RE remained almost constant at 15%.

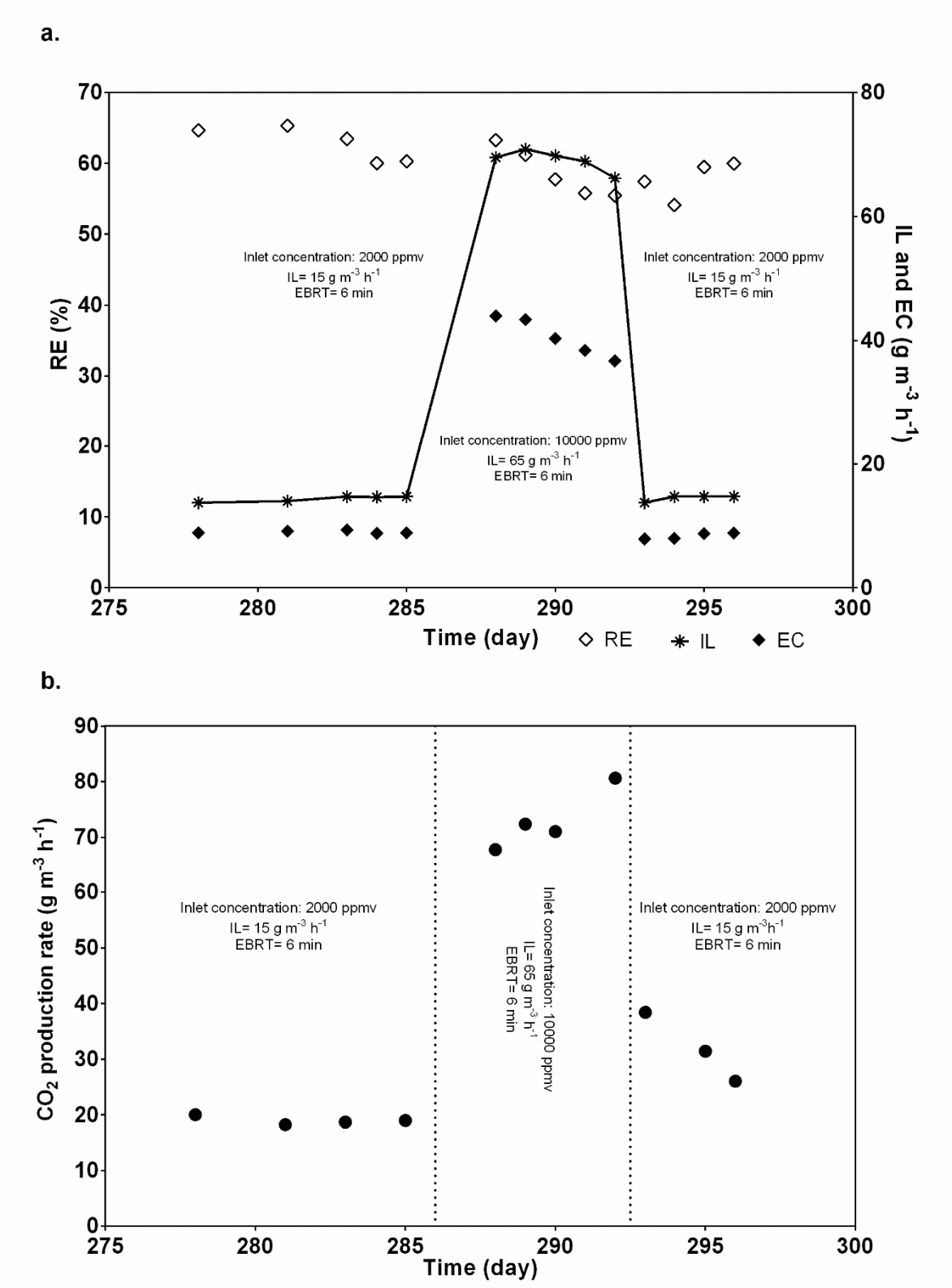

Figure 3.5: Shock loads by inlet concentration sudden variation: a. Conversion, elimination capacity and inlet load as a function of time, b. Carbon dioxide production rate as a function of time

The drastic decrease of RE could be related to the shorter EBRT of 1 min which significantly reduced the contact time between CH_4 and the biofilm phase and caused mass transfer limitations [67]. The EC was not significantly influenced by the shock load and remained at 10 g m^{-3} h^{-1}. Nikiema and Heitz (2009) [104] indicated the CH_4 mass transfer limitations were more significant on the biofilter performance when gas flow rate was decreased, rather than biological reaction limitations. Kraakman et al. (2011) [18] also reported the gas-biofilm contact time as a critical factor for CH_4 in biofilters.

Figure 3.6b shows the CO_2 production rate when the shock load was applied by the gas flow rate. The CO_2 production rate increased from 18 to 22 g m^{-3} h^{-1} when the gas flow rate was increased from 3 to 15 L min^{-1}. The PCO_2 improvement from 20 to 72 g m^{-3} h^{-1} (260% improve) for inlet concentration variation (Figure 6a) was higher than the PCO_2 improvement from 18 to 22 g m^{-3} h^{-1} (22% improve) when the same shock load of IL from 13 to 65 g m^{-3} h^{-1} was applied by gas flow rate variation (Figure 6b). Higher PCO_2 improvement in Figure 6a could be explained by the fact that short EBRTs do not provide enough time for CH_4 biological degradation to occur [67, 104]. The degree of mineralization of CH_4 (mole of CO_2 production based on one mole of CH_4 consumption) gives a better understanding of the effect of each shock loads on the biofilter behavior. In this study, for shock load by inlet concentration; PCO_2/EC and degree of mineralization were decreased from 2.22 to 1.67 and from 0.8 to 0.6 respectively. Therefore, during the shock load, the biodegradation of CH_4 was in the favor of 25% higher biomass production for one mole of CH_4 consumption. This was in agreement with the excess biomass growth which was observed visually and the RE decrease from 65 to 55%. On the other hand, shock load by flow rate ended up to an increase of PCO_2/EC and degree of mineralization from 1.8 to 2.2 and 0.65 to 0.8 which shows approximately an opposite behavior of the biofilter compared to the shock load by inlet concentration variation. Thus, during shock load by flow rate, the biofilter tended to produce higher amount of CO_2 rather than biomass. Figures 5 and 6 show that when the IL was brought back to its original value, the biofilter responses were quite rapid because the RE and EC returned to their initial values. Nevertheless, to our best knowledge, no study has investigated the transient behavior of a CH_4 biofilter.

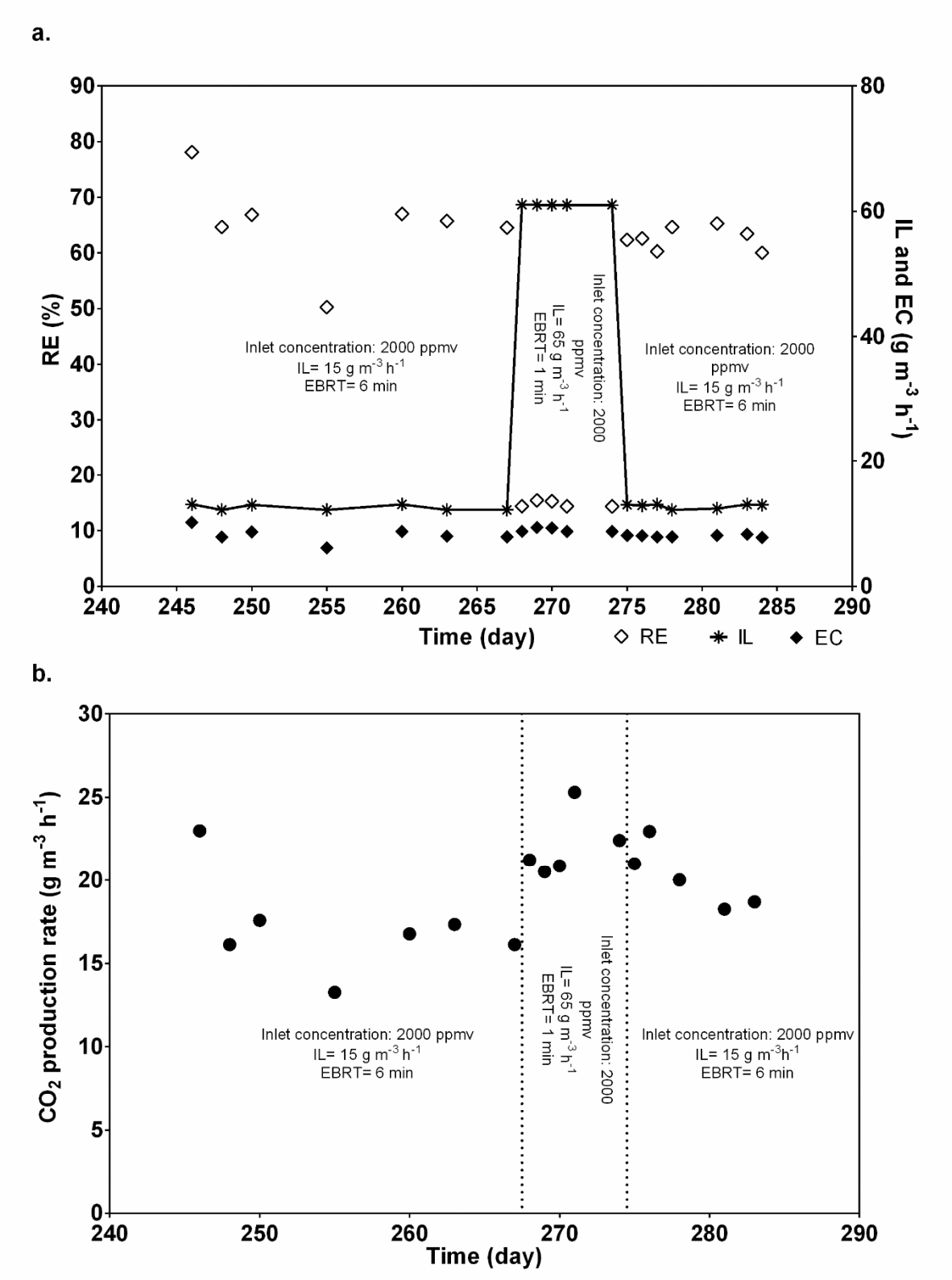

Figure 3.6: Shock loads by CH_4 flow rate sudden variation: a. Conversion, elimination capacity and inlet load as a function of time, b. Carbon dioxide production rate as a function of time

3.5.3 Starvation

Figure 3.7a shows the performance of the biofilter under different conditions of starvation. Before the starvation (IL = 13 g m^{-3} h^{-1}, inlet concentration = 2000 ppmv, EBRT= 6 min), the average RE and EC were around 75% and 11 g m^{-3} h^{-1} respectively. The nutrient solution addition was stopped for 14 days (days 338-352, step 1). During step 1, the average RE was improved to 80%. Basically, without nutrient solution addition, the biofilm may get thinner and provide less resistance for hydrophobic pollutant mass transfer [88]. Therefore, in the present study, the mass transfer of CH_4, a hydrophobic compound, could be enhanced for a few days owing to a thinner biofilm. The lack of nutrient solution for 14 days did not reduce the performance of the biofilter. In other words, the addition of nutrient solution once every two weeks could be sufficient for the biofilter. Nikiema and Heitz (2010) [77] eliminated the nutrient solution irrigation to a rock filter-bed (void fraction of 0.37) used for CH_4 biofiltration with no interruption in humid gas flow rate of 5.5 L min^{-1} and CH_4 inlet concentration of 3500 ppmv. They reported a reduction of RE from 63 to 35% after 7 days of starvation.

After 14 days of nutrient starvation, 1.5 L of tap water without nutrients was added to the biofilter for 1 min once per day (step 2). For the following 14 days (days 352-366), introducing tap water instead of nutrient solution diminished the RE from 80 to 73%. The water irrigation might wash out a fraction of the nutrients on the packing material and as a result the level of nutrient diminished. Consequently, the remaining nutrients were not sufficient to keep the original RE of 80%. However, these two following steps of starvation did not destroy the microbial culture in the biofilter as the RE only decreased to 73%. However, Nikiema and Heitz (2010) [77] reported the absence of nutrient solutions could drop a CH_4 biofilter performance after 7 days from 63 to 35%. The stone used as a packing material with a void space volume of 0.43 in the present study, seemed to be more capable of holding nutrients and water for a longer period compared to other rock materials.

The last step of the starvation (step 3) was performed from days 366 to 395 by continuing to feed humid air to the biofilter without any CH_4 and nutrient solution addition. After 30 days of starvation, IL was reset to 13 g m^{-3} h^{-1}. The results before and after 30 days without CH_4 and nutrients showed that the conversion dropped from 70 to 10% for an IL of 13 g m^{-3} h^{-1}. The significant decrease of RE and EC after 1 month, can be explained by low water affinity of CH_4 [21].

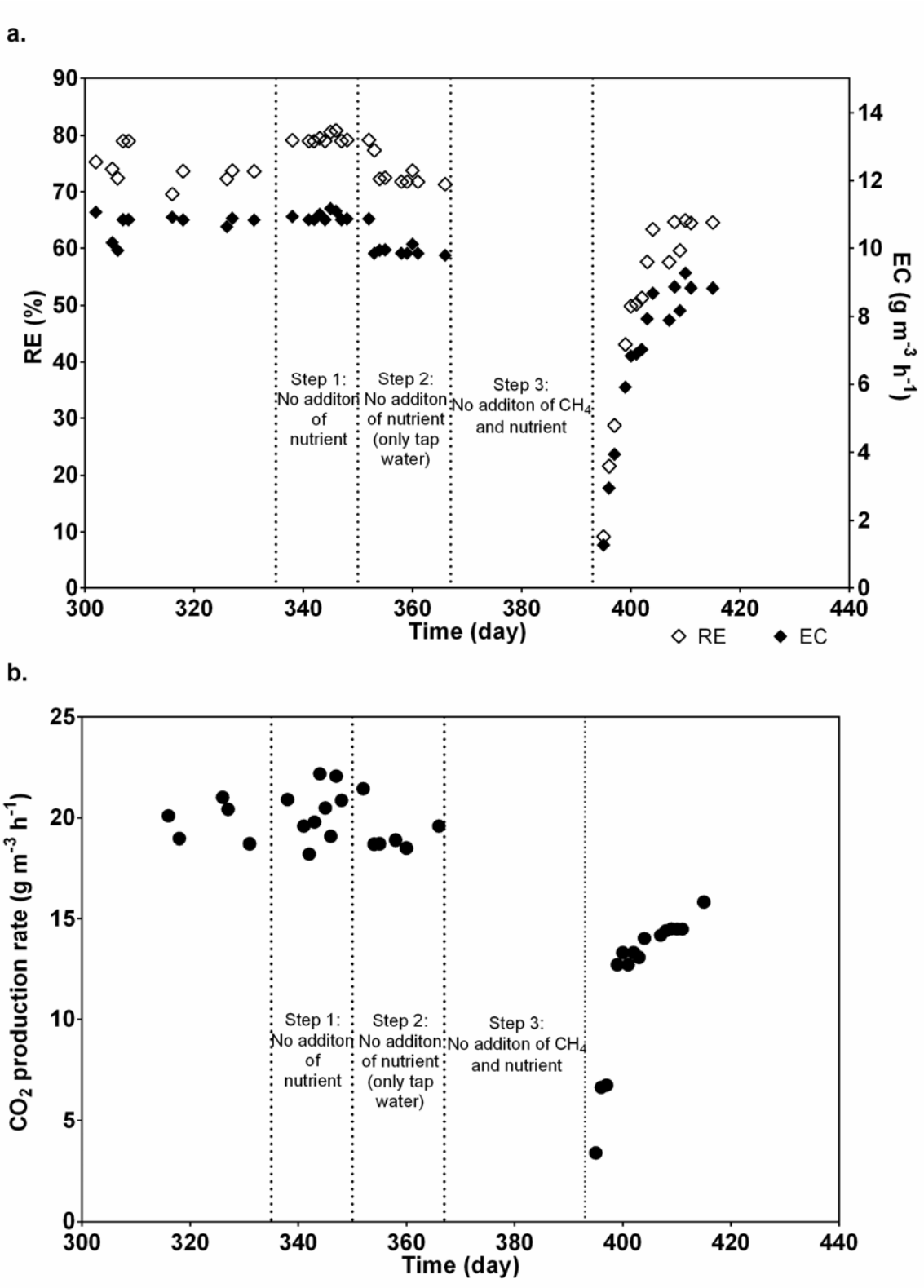

Figure 3.7: Effect of starvations on the biofilter performance for a constant IL of 13 g m^{-3} h^{-1}: a. Biofilter conversion and elimination capacity as a function of time, b. Carbon dioxide production rate as a function of time

In this case, the biofilm ran out of CH_4 very quickly despite some hydrophilic pollutants like styrene that can be remained in the biofim during starvation for a few days [98]. Therefore, the unavailability of CH_4 in the biofilm could reduce the microbial activities. In addition, after the IL resumption, the EC improved from 1 to 7 g m^{-3} h^{-1} during days 395 to 400. Nevertheless, the recovery of the biofilter was relatively rapid and after 5 days (days 395 to 400), the RE reached 50%. For the following 15 days, the biofilter conversion improved to 65%. Figure 3.7b presents the CO_2 production rate for the corresponding starvation steps. For steps 1 and 2, there were some slight variations of CO_2 production rate (20 ± 1 g m^{-3} h^{-1}) showing that biological reactions continued with no nutrient solution addition. However, at step 3 of starvation (30 days), the CO_2 production dropped from 20 to 4 g m^{-3} h^{-1} (days 366 to 395). Therefore, after 1 month, the shortage of CH_4 reduced the activity of the biofilm. According to Figures 3.7a and b, 5 days (days 395 to 400) were needed for the microbial population to be developed and to reach approximately the original performance of the biofilter.

3.5.4 Conclusion

The aim of present study was to evaluate a) the performance of a stone-based bed bioflter for abatement of different CH_4 inlet concentrations in the range of 1000 to 13000 ppmv under pseudo steady state conditions as well as b) the biofilter behavior under different shock load strategies and starvations. The biofilter performance for CH_4 elimination in the range from 1000 to 4000 ppmv was reliable with a corresponding variation of RE from 87 to 75%. However, CH_4 inlet concentrations exceeding 4000 ppmv to 13000 ppmv could significantly reduce the conversion from 75 to 52% due to some biofilm reaction limitations. In addition, increasing the value of PCO_2/EC from 1.8 to 2.4 was in the agreement of higher ratio of CO_2 in end products when the EC increased from 10 to 45 g m^{-3} h^{-1}.

In the case of transient state, the biofilter was quite flexible in both types of shock loads (sudden variations of inlet concentration or gas flow rate) and responded quickly. Methane and nutrient starvations were performed in three steps. The biofilter operated with no nutrient (step 1) and only tap water without nutrient (step 2), respectively. In step 3, both CH_4 and nutrient addition were removed from the biofilter. The results show a promising potential of the biofilter to overcome the lack of nutrient solution (steps 1, 2). Only passage of humid air without CH_4 and

without nutrient for 1 month (step 3) was a harsh condition for the biofilter and resulted in a decline of biofilter conversion from 70 to 10%.

3.5.5 Acknowledgments

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CHAPTER 4. Steady state and dynamic behaviors of a methane biofilter under periodic addition of ethanol vapors

Avant propos:

L'article "Steady state and dynamic behaviors of a methane biofilter under periodic addition of ethanol vapors*"* a été publié dans le Journal "*Environmental Management*" 197 (2017) 106-113.

TITRE: Comportement en régimes permanent et transitoire d'un biofiltre traitant le méthane en présence d'éthanol

Title: Steady state and dynamic behaviors of a methane biofilter under periodic addition of ethanol vapors

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Contribution to the document: This paper is relevant to the second objective of the thesis. The steady state and transient state performance of a CH_4 biofilter under periodic addition of ethanol and under different gas flow rates was studied. The sensitivity of the biofilter to intermittent ethanol addition and the biofilter recovery after each period of ethanol addition were discussed.

Steady state and dynamic behaviors of a methane biofilter under periodic addition of ethanol vapors

4.1 Résumé

De l'éthanol a été ajouté au méthane (CH_4) dans un biofiltre ayant un lit inorganique sur 3 cycles en augmentant par paliers le débit volumique de 3 à 6 et à 12 L min^{-1} ce qui correspond à des temps de résidence en fût vide (EBRT) de 6, 3 et 1.5 min. La performance en régime permanent du biofiltre traitant le CH_4 a été étudiée pour des charges à l'entrée de CH_4 de 33, 66 et 132 g_{CH4} m^{-3} h^{-1} avant et après les cycles d'ajout d'éthanol. De plus, la conversion en régime permanent d'un mélange gazeux CH_4 et éthanol, pour un ratio massique CH_4/éthanol =7.5 g $_{CH4}$ $g_{éthanol}^{-1}$ a été évaluée sur 3 cycles (EBRT de 6, 3 et 1.5 min). En absence d'éthanol, la conversion (RE) du CH_4 a diminué de 35 à 7 % suite à la diminution de l'EBRT de 6 à 1.5 min. De plus, la présence d'éthanol diminue la conversion du CH_4 pour un EBRT constant dans chaque cycle. La conversion du CH_4 a diminué de 35 à 29 %, de 17 à 13 % et de 7 à 0 % pour des charges à l'entrée de 4.5, 9 et 18 $g_{éthanol}$ m^{-3} h^{-1} sur les 3 cycles. De plus, la présence périodique d'éthanol dans le biofiltre traitant le CH_4 a permis l'étude du comportement en régime transitoire du biofiltre pendant l'ajout d'éthanol ainsi que la récupération du biofiltre après chaque cycle . La diminution de la conversion du CH_4 suite à l'ajout d'éthanol dans chaque cycle fut instantanée. Cependant, la récupération de la conversion du CH_4 après l'arrêt d'ajout d'éthanol a pris 10, 14 et 25 jours pour des charges à l'entrée d'éthanol de 4.5, 9 et 18 $g_{éthanol}$ m^{-3} h^{-1} respectivement. La période de récupération était reliée à la concentration d'éthanol dans le lixiviat qui était respectivement de 1100 ± 200, 1100 ± 350 et 2500 ± 400 $g_{éthanol}$ $m^{-3}_{lixiviat}$ pour des charges à l'entrée d'éthanol de 4.5, 9 and 18 $g_{éthanol}$ m^{-3} h^{-1}. En fonction du comportement en régimes permanent et transitoire, le débit volumique le plus faible de 3 L min^{-1} (EBRT de 6 min) était la condition opératoire la plus appropriée en présence des deux polluants (charge à l'entrée de CH_4 de 33 g_{CH4} m^{-3} h^{-1} et charge à l'entrée d'éthanol de 4.5$g_{éthanol}$ m^{-3} h^{-1}).

Mots clefs : Biofiltre, méthane, éthanol, mélange, sensibilité, débit volumique.

4.2 Abstract

Ethanol was added to a methane (CH_4) biofilter with inorganic packing materials over three cycles based on increasing the gas flow rates from 3 to 6 and finally to 12 L min^{-1} corresponding to empty bed residence times (EBRT) of 6, 3 and 1.5 min. The steady state performance of the CH_4 biofilter was studied for CH_4 inlet loads (ILs) of 33, 66 and 132 g_{CH4} m^{-3} h^{-1} prior and after each ethanol cycle. In addition, the steady state removal of a mixture of CH_4 and ethanol for a CH_4/ethanol mass ratio of around 7.5 g_{CH4} $g_{ethanol}^{-1}$ was evaluated over three cycles (EBRTs of 6, 3 and 1.5 min). In the absence of ethanol, the CH_4 removal efficiency (RE) dropped from 35 to 7% due to an EBRT decrease from 6 to 1.5 min. In addition, the presence of ethanol resulted in a CH_4 RE reduction at a constant EBRT in every cycle. The CH_4 REs dropped from 35 to 29%, 17 to 13% and 7 to 0% for corresponding ethanol ILs of 4.5, 9 and 18 $g_{ethanol}$ m^{-3} h^{-1} over the cycles. Moreover, the periodic presence of ethanol in the CH_4 biofilter allowed the study of transient behaviors of the biofilter during ethanol addition and the biofilter recovery after each cycle. The CH_4 RE reductions as a result of ethanol addition in each cycle were instantaneous. However, the CH_4 RE recovery after completion of ethanol addition took 10, 14 and 25 days for ethanol ILs of 4.5, 9 and 18 $g_{ethanol}$ m^{-3} h^{-1} respectively. The recovery time was related to the ethanol concentration in the leachate which were 1100 ± 200, 1100 ± 350 and 2500 ± 400 $g_{ethanol}$ $m^{-3}_{leachate}$ for corresponding ethanol ILs of 4.5, 9 and 18 $g_{ethanol}$ m^{-3} h^{-1}, respectively. Based on steady state and dynamic process conditions of the biofilter, the lowest gas flow rate of 3 L min^{-1} (EBRT of 6 min) produced the best performance when both pollutants were present (CH_4 IL of 33 g_{CH4} m^{-3} h^{-1} and ethanol IL of 4.5 $g_{ethanol}$ m^{-3} h^{-1}).

Keywords: Biofilter, methane, ethanol, mixture, sensitivity, gas flow rate

4.3 Introduction

Over the recent years, greenhouse gas (GHG) emissions of methane (CH_4) and carbon dioxide (CO_2) have been targeted for reduction due to their global warming effects [153]. At a recent climate change conference (COP 21, Paris 2015), more than 200 countries submitted an agreement to keep the global temperature from increasing more than 2˚C compared to pre-industrial levels [1]. Methane, the second most important GHG, accounts for 16% of total GHG emissions in the world [154]. The impact of CH_4 on climate change is 25 times higher than CO_2

over a 100 years time frame [2]. Anthropogenic activities like landfills, energy sectors (e.g., natural gas refineries) and anaerobic wastewater treatment units contribute to 60% of the global CH_4 emissions worldwide [3]. Methane elimination in biofilters is an appropriate technique for CH_4 concentrations below 3% (v/v) [4]. In a biofilter, CH_4 is transferred from gas to biofilm phase to be degraded into less hazardous components like CO_2, water and biomass through biological reactions [14]. An important future challenge for CH_4 biological elimination is the stability of CH_4 biofilters [94]. Factors such as a sudden inlet load (IL)'s variations or periodic absence of CH_4 can disturb the stability of the biofilter and leads to poor performance during transients [56]. In this regard, the periodic addition of a second pollutant like ethanol vapors to a CH_4 biofilter may also disturb the stability of the biofilter. Few studies used biofilters for a mixture of the gaseous pollutants [3]. However, emissions with multiple pollutants is a common situation in industries [57]. The CH_4 leakage from anaerobic wastewater treatment plants of food industries can include ethanol [2]. Ethanol is also considered a hazardous component for humans and targeted for removal in biofilters [54, 120].

Unlike CH_4 which has poor solubility (dimensionless Henry's law constant of 28 at 25 ˚C, P=1 atm) [6], ethanol is completely miscible with water with a low dimensionless Henry's law constant (0.002 at 25 ˚C, P=1 atm). Therefore, ethanol is more readily bioavailable in the biofilm phase compared to CH_4 under a similar condition in the biofilters [5]. Ethanol biofilters are usually subjected to EBRTs shorter than 1 min [120]. In contrast, EBRTs longer than 4 min for CH_4 biofilters can provide sufficient contact time between CH_4 and the biofilm phase and can increase the bioavailability of CH_4 in biofilm [110, 155].

Although a number of studies focused on the removal of CH_4 or ethanol in biofilters, to our best knowledge no study has looked at steady state and dynamic behaviors of biofilters when the both pollutants are present. Therefore, the steady state performance of the biofilter should be studied in order to choose an appropriate EBRT when CH_4 and ethanol are fed simultaneously is necessary to be examined. On the other hand, the dynamic behaviors of a CH_4 biofilter under periodic presence of ethanol at different EBRTs gives a better understanding about the phenomena happening during the pollutants removal. Because of the low ethanol dimensionless Henry's law constant of 0.002, a fraction of the inlet ethanol may dissolve in the biofilm phase and is subsequently drained as lixiviate [55]. If the ethanol absorption exceeds the ethanol biodegradation, a dynamic equilibrium based on the ethanol accumulation can occur in the

biofilm phase during ethanol biofiltration. On the other hand, when the ethanol addition is completed, the residue of the accumulated ethanol likely delays the recovery of the biofilter. Therefore, the dynamic response of the biofilter in gas phase during ethanol addition and ethanol addition completion, may be related to the dynamic equilibrium between gas and biofilm phase via ethanol absorption.

The present study aimed to investigate the steady state performance and transient behavior of a biofilter for CH_4 removal under periodic ethanol loadings. The effect of gas flow rate on the biofilter performance was studied for individual CH_4 removal as well as during elimination of a vapor mixture of CH_4 and ethanol. The continuous loading of CH_4 under ethanol intermittent loading may cause unfavorable transient conditions for the biofilter. In this case, the biofilter dynamic responses during ethanol addition as well as the biofilter recovery when ethanol addition stopped were studied.

4.4 Materials and methods

4.4.1 Experimental setup

Figure 4.1 shows a schematic flow chart of the biofilter. The biofilter was made of Plexiglas with a diameter of 0.15 m and a total height of 1 m. The biofilter included three equal sections to provide a total volume of $18*10^{-3}$ m^3. An inorganic material with an average diameter of $12*10^{-3}$ m and a specific surface area of 310 m^2 m^{-3} was used as support media. The exact nature of the packing materials cannot be disclosed due to a confidential agreement. The gas samples including CH_4, ethanol and CO_2 were collected from four gas sampling ports along the biofilter. The feed to the up-flow biofilter was a mixture of CH_4, humid air and ethanol. Methane stream was provided from a CH_4 cylinder (Praxair Inc., Canada) with a regulated pressure of 275 kPa. Humid air and ethanol vapors were produced from a humidifier and an ethanol bubbler respectively. The nutrient solution addition was fed for 1 min every day at a flow rate of 1.5 L min^{-1} in order to provide essential nutrients like nitrogen, phosphorous, potassium and copper for the biofilter's microbial culture. The characteristics of the nutrient solution were similar to the one used by Ménard et al. (2012) [151].

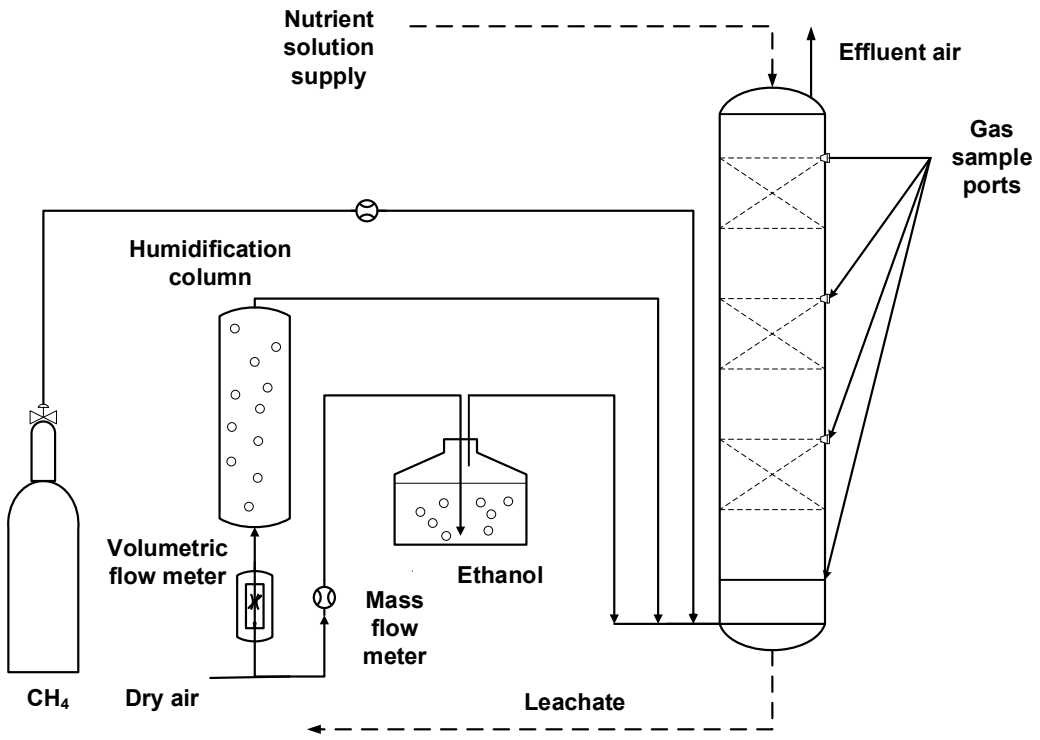

Figure 4.1: Experimental schematic of the biofilter

4.4.2 Microbial culture

The biofilter had been used for CH_4 elimination during 4 months (unpublished data). After a one week shutdown, the biofilter was restarted in order to begin the present study. Therefore, the microbial culture in the biofilter was already adapted to CH_4 removal. The initial source of inoculation was from the leachate of a CH_4 biofilter [56].

4.4.3 Analytical methods

Methane and ethanol vapors concentration were measured by a total hydrocarbon analyzer (FIA 510, Horiba, USA). To analyze the pollutant's mixture, after measuring the total hydrocarbon concentration, CH_4 was temporarily removed from the biofiter and the ethanol concentration was measured. The CH_4 concentration was considered as the difference between the total hydrocarbon and ethanol concentrations. The CO_2 concentrations were determined by a CO_2 gas analyzer (Ultramat 22P, Siemens, Germany). The ethanol concentrations in the leachate were analyzed using total organic carbon analyzer (TOC-V_E, Shimadzu, Japan).

4.4.4 Performance parameters

The performance of the biofilter was quantified by removal efficiency (RE), inlet load (IL), elimination capacity (EC) and CO_2 production rate (P_{CO_2}) as described below:

Removal efficiency (RE)	$\frac{(C_{Gi} - C_{Go})}{C_{Gi}} \times 100$	(%)
Inlet load (IL)	$\frac{Q \times C_{Gi}}{V_{bf}}$	(g m^{-3} h^{-1})
Elimination capacity(EC)	$\frac{(C_{Gi} - C_{Go}) \times Q}{V_{bf}}$	(g m^{-3} h^{-1})
CO_2 production rate (P_{CO_2})	$\frac{(CO_{2_{Out}} - CO_{2_{in}}) \times Q}{V_{bf}}$	(g m^{-3} h^{-1})

In the equations above, C_{Gi} and C_{Go} are the inlet and outlet pollutants concentration ($g_{CH_4} m^{-3}$ or $g_{ethanol}$ m^{-3}) respectively, V_{bf} is the biofilter volume (m^3), Q is the gas flow rate (m^3 h^{-1}), $CO_{2_{in}}$ and $CO_{2_{Out}}$ are the concentrations of CO_2 ($g_{CO_2} m^{-3}$) regarding to inlet and outlet of the biofilter respectively.

4.4.5 Methodology and experimental conditions

Table 4.1 summarizes the operating conditions and experimental steps of the biofilter. The biofilter ran under three different EBRTs of 6, 3 and 1.5 min corresponding to gas flow rates of 3, 6 and 18 L min^{-1} respectively for a period of 281 days. The CH_4 ILs were 33, 66 and 132 g_{CH4} m^{-3} h^{-1} corresponding to the EBRTs. Ethanol with an average concentration of 0.45 $g_{ethanol}$ m^{-3} was introduced to the biofilter at three separate cycles based on EBRTs of 6, 3 and 1.5 min with corresponding ILs of 4.5, 9 and 18 $g_{ethanol}$ m^{-3} h^{-1} respectively. The CH_4 and ethanol inlet concentrations were fixed at 3.4 g_{CH4} m^{-3} and 0.45 $g_{ethanol}$ m^{-3} respectively to obtain a CH_4/ethanol mass ratio of 7.5 g_{CH4} $g_{ethanol}^{-1}$ in each cycle. Prior to cycle 1 in the absence of ethanol, the biofilter started with CH_4 at an IL of 33 g_{CH4} m^{-3} h^{-1} and an EBRT of 6 min (precycle 1). Subsequently, the first cycle of ethanol addition to the CH_4 biofilter was performed at an ethanol IL of 4.5 $g_{ethanol}$ m^{-3} h^{-1} under the EBRT of 6 min (cycle 1). Finally, before moving to the next EBRTs, ethanol was removed in order to study the CH_4 biofilter performance after

cycle 1 (post cycle 1). The evolution of the biofilter continued with a similar method for decreasing EBRTs to 3 and 1.5 min.

Table 4.1: Experimental conditions

Gas flow rate ($L\ min^{-1}$)	EBRT (min)	Steps	Time (days)	Methane IL ($g\ m^{-3}\ h^{-1}$)	Ethanol IL ($g\ m^{-3}\ h^{-1}$)
3	6	Pre cycle 1	1-71	33	-
		Cycle 1	72-124	33	4.5
		Post cycle 1	125-136	33	-
6	3	Pre cycle 2	137-145	66	-
		Cycle 2	146-170	66	9
		Post cycle 2	171-185	66	-
12	1.5	Pre cycle 3	186-204	132	-
		Cycle 3	205-253	132	18
		Post cycle 3	254-281	132	-

Therefore, the biofiler steady state performance was studied through 9 steps identified as precycles, cycles and post cycles of ethanol addition for three EBRTs. In addition, the ethanol concentration in the leachate in each cycle was periodically measured.

The transient state performance of the biofilter was studied during each cycle as well as when the ethanol feeding was stopped. During every cycle, the dynamic behavior of the biofilter performance was evaluated in terms of CH_4 REs until reaching steady state conditions. When each cycle was finished, the resumption of the biofilter was investigated until biofilter returned its initial performance. After each cycle, ethanol might still exist in the biofilm phase. Therefore, the leachate analyze continued during the recovery time until the leachate became was almost free of ethanol.

4.5 Results and discussion

4.5.1 The biofilter's overall performance

Figure 4.2a shows the biofilter performance for CH_4 removal in the cyclic presence of ethanol for a constant CH_4 inlet concentration of 3.4 g_{CH4} m^{-3} during 281 days of operation. According to Figure 4.2a, the CH_4 RE dramatically dropped from 35 ± 3.5% to 7 ± 1% when the CH_4 IL increased from 33 to 132 g_{CH4} m^{-3} h^{-1} as a result of an EBRT reduction from 6 to 1.5 min. According to the CH_4 mass transfer limitations and thermodynamic equilibrium (low water solubility of CH_4), decreasing EBRT provided shorter contact time between the gas and biofilm phase to establish a gas-liquid equilibrium and reduced the biofilter performance [110].

Methane biofilters frequently operate at constant EBRTs longer than 4 min and ILs lower than 100 g_{CH4} m^{-3} h^{-1} [110, 155] in order to overcome mass transfer and thermodynamic equilibrium limitations [27]. A few studies investigated the performance of a CH_4 biofilter at different EBRTs mainly long EBRTs (longer than 6 min) out of the range of this study [156]. The decreasing trend of RE as a function of EBRT in the present study was in accordance with Nikiema and Heitz (2009) [104] results when the RE in a CH_4 biofilter diminished from 55 to 35% for an IL increasing of 33 to 66 g_{CH4} m^{-3} h^{-1} as a result of an EBRT variation in the range of 3 to 6 min. Park et al. (2009) [67] evaluated the effect of EBRT in the range of 5 to 70 min corresponding to ILs of 55 to 557 g_{CH4} m^{-3} h^{-1} in a CH_4 biofilter. The minimum RE of 20% was obtained for the shortest EBRT of 5 min and an IL of 557 g_{CH4} m^{-3} h^{-1}.

Prior to cycle 1, the biofilter was fed with only CH_4 with an IL of 33 g_{CH4} m^{-3} h^{-1} with an EBRT of 6 min for 71 days to ensure the steady state performance of the biofilter before ethanol addition. The average CH_4 RE was 35 ± 3.5% before the first cycle of ethanol addition. However, when the CH_4 biofilter was exposed to ethanol with an IL of 4.5 $g_{ethanol}$ m^{-3} h^{-1} in cycle 1, the CH_4 RE dropped from 35 ± 3.5% to 29 ± 1% (total IL of 38 $g_{ethanol+CH4}$ m^{-3} h^{-1}).

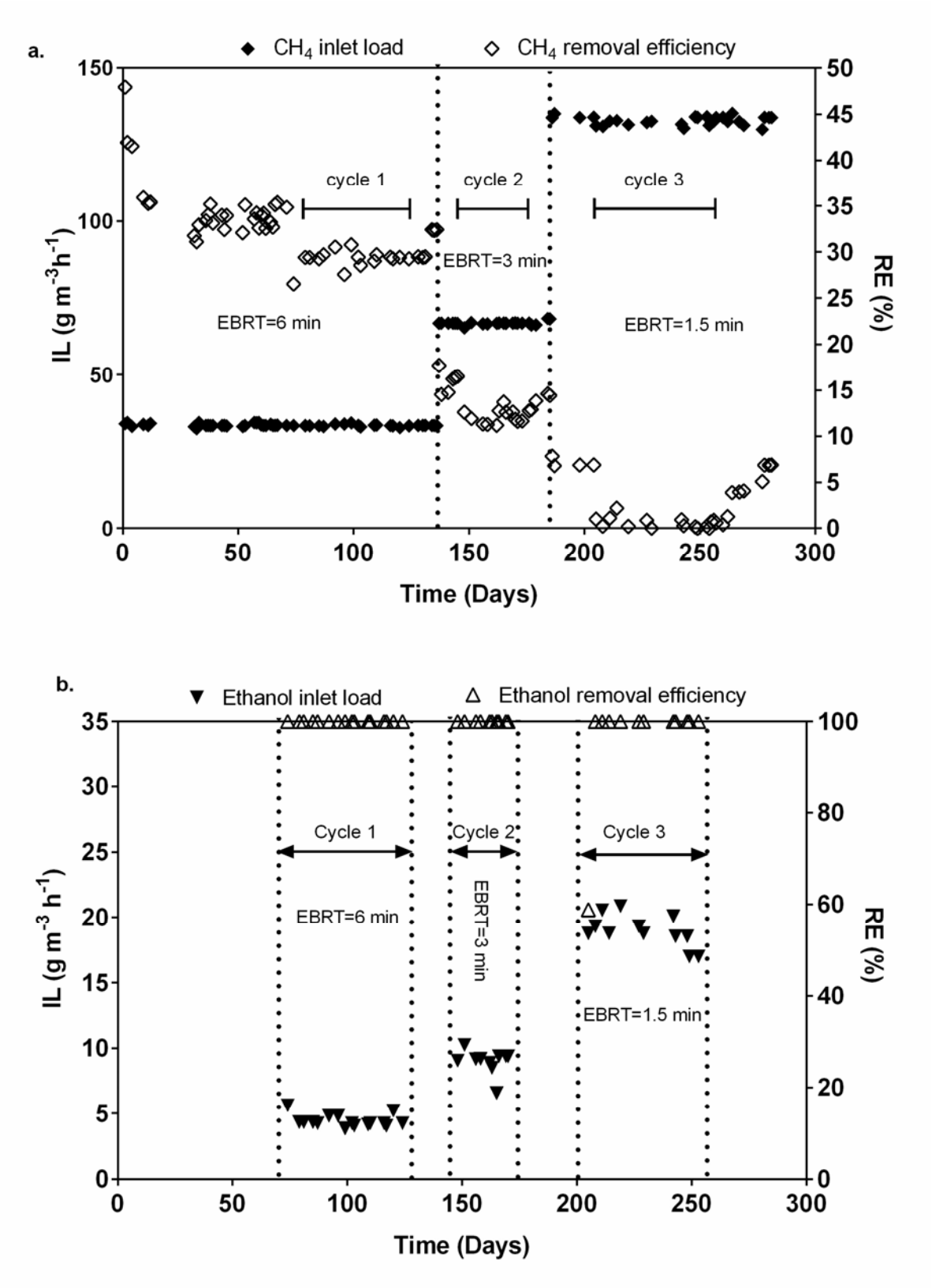

Figure 4.2 : The overall performance of the biofilter: a. CH_4; b. Ethanol

The CH_4 RE reduction could be attributed to the toxic effects of ethanol on methanotrophs [157]. In addition, in the presence of CH_4 and ethanol, the alcohol might be consumed preferentially by the microbial culture [157]. The addition of ethanol over cycles 2 and 3 had a similar effect on CH_4 elimination. According to Figure 2a, before cycles 2 and 3, the biofilter operated under steady state condition with a CH_4 RE of 17 ± 1% and 7 ±1% for a CH_4 IL of 66 and 132 g_{CH4} m^{-3} h^{-1} respectively. When an ethanol IL of 9 $g_{ethanol}$ m^{-3} h^{-1} was applied during cycle 2, the CH_4 RE diminished from 17 ± 1% to 12 ± 1%. In cycle 3, ethanol was fed with an IL of 18 $g_{ethanol}$ m^{-3} h^{-1} and stopped CH_4 elimination such that CH_4 RE fell down from 7 ± 1% to 0 ± 1% under a CH_4 IL of 132 g_{CH4} m^{-3} h^{-1} (days 204 to 253). The percentage of CH_4 RE decrease in cycles 1, 2 and 3 were respectively 17, 23 and 100% for corresponding EBRTs of 6, 3, and 1.5 min respectively. Therefore, under the shortest EBRT of 1.5 min, the CH_4 RE decrease was more significant (100% of its original value of 7± 1%) such that CH_4 RE declined to 0%. This could be explained by the fact that an EBRT of 1.5 min (ethanol IL as 18 $g_{ethanol}$ m^{-3} h^{-1}, CH_4 IL of 132 g_{CH4} m^{-3} h^{-1}), compared to an EBRT of 6 min (ethanol IL as 4.5 $g_{ethanol}$ m^{-3} h^{-1}, CH_4 IL of 33 g_{CH4} m^{-3} h^{-1}) caused additional toxic effects for methanotrophs. Figure 4.2b shows the individual REs of ethanol corresponding to ethanol ILs ranging from 4.5 to 18 $g_{ethanol}$ m^{-3} h^{-1} in cycles 1 to 3 of ethanol addition for an ethanol inlet concentration of 0.45 $g_{ethanol}$ m^{-3}. According to Figure 4.2b, complete removal of ethanol (RE=100%) was obtained in every cycle. Therefore, neither the presence of CH_4 nor the EBRT variation affected the removal of ethanol in the biofilter. Unlike CH_4, there is no limitation for ethanol solubility in the biofilm phase since ethanol is miscible with water [5]. Ethanol was removed completely (RE of 100%) in biofilters for ILs up to 100 $g_{ethanol}$ m^{-3} h^{-1} under EBRTs shorter than 1 min [54, 120].

4.5.2 Global and individual ECs

Figure 4.3 shows the total EC as well as individual CH_4 and ethanol ECs as a function of total ILs during cycles 1, 2 and 3. The total ILs during cycles 1, 2 and 3 were 38, 75 and 152 $g_{ethanol+CH4}$ m^{-3} h^{-1} respectively. According to Figure 4.3, increasing the total ILs reduced the CH_4 ECs from 10 to 8 and from 8 to 0 g_{CH4} m^{-3} h^{-1} by moving from cycle 1 to cycle 2 and from cycle 2 to cycle 3 respectively. The CH_4 ECs versus total ILs exhibited a nonlinear decreasing trend. The negative slopes between cycle 1 and cycle 2 and cycle 2 and cycle 3 were 0.05 and 0.1 respectively. Thus, the decreasing trends of CH_4 ECs for a total IL variation from 75 to 152

$g_{ethanol+CH4}$ m^{-3} h^{-1} was 2 fold greater compared to a total IL variation ranging from 38 to 75 $g_{ethanol+CH4}$ m^{-3} h^{-1}. Increasing CH_4 ILs with gas flow rate at a constant CH_4 inlet concentration leads to a CH_4 EC reduction as a result of an EBRT decline. Since CH_4 is poorly soluble in water, EBRTs less than 6 min might provide inadequate CH_4-biofilm contact time for an appropriate CH_4 mass transfer from gas to the biofilm phase in biofilters. Park et al. (2009) [67] observed a CH_4 EC decline from 280 to 200 g_{CH4} m^{-3} h^{-1} related to a CH_4 IL increase from 400 to 550 g_{CH4} m^{-3} h^{-1} with a gas flow rate increase from 1 to 2 L min^{-1} (an EBRT variation from 5.1 to 3.9 min and a CH_4 inlet concentration of 35 g_{CH4} m^{-3}).

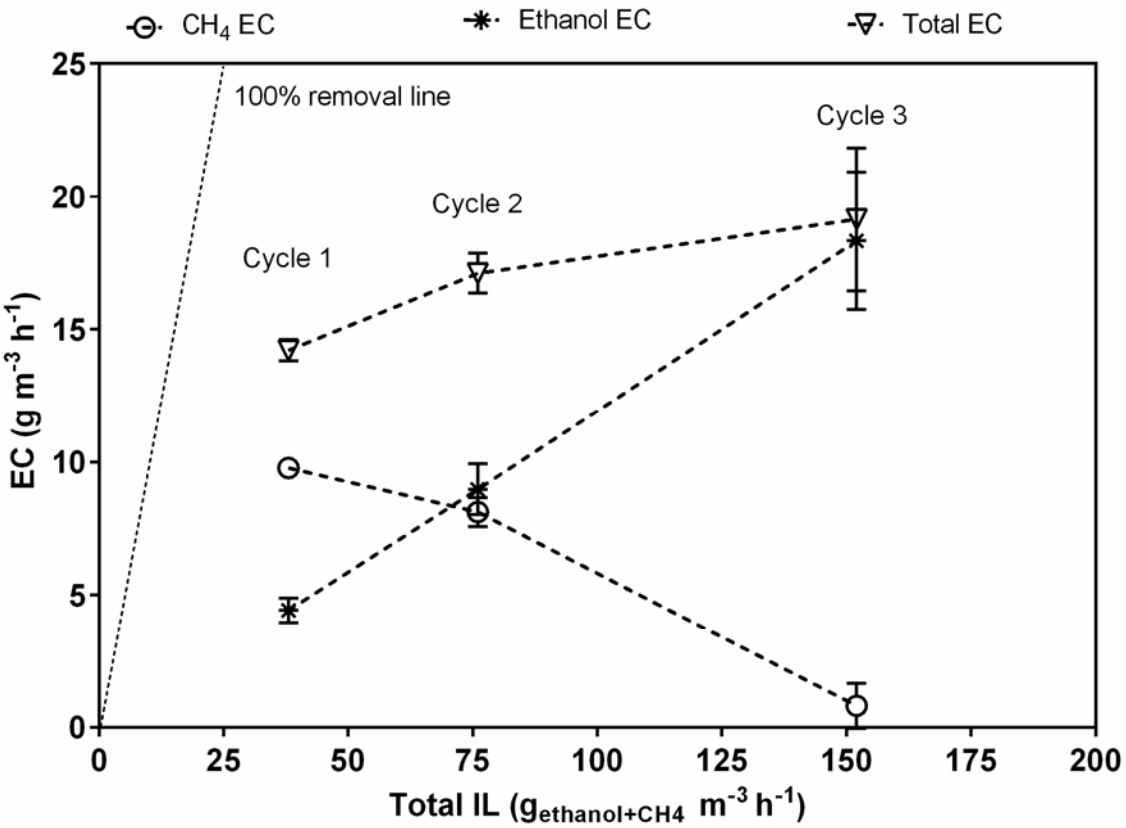

Figure 4.3: The global and individual ECs as a function of total IL

According to Figure 4.3, ethanol ECs showed an opposite trend compared to CH_4 ECs. When the total IL increased from 38 to 152 $g_{ethanol+CH4}$ m^{-1} h^{-1}, the ethanol ECs increased linearly from 4 to 18 $g_{ethanol}$ m^{-3} h^{-1}. Christen et al. (2002) [54] reported an increasing ethanol EC from 90 to 110 $g_{ethanol}$ m^{-1} h^{-1} in a biofilter when the ethanol IL increased from 90 to 150 $g_{ethanol}$ m^{-1} h^{-1} (an EBRT reduction from 6 to 3 min and a constant ethanol inlet concentration of 9 g m^{-3}).

According to Figure 4.3, although the CH_4 ECs declined from 10 to 0 g_{CH4} m^{-3} h^{-1} over cycles 1 to 3, the total ECs improved from 14 to 18 $g_{ethanol+CH4}$ m^{-3} h^{-1} due to the ethanol ECs improvement from 4 to 18 $g_{ethanol}$ m^{-3} h^{-1}. In addition, the deviation of the total ECs from the RE line of 100% became more significant when the total IL increased from 38 to 152 $g_{ethanol+CH4}$ m^{-3} h^{-1} through the cycles. The deviation at cycle 3 was the most significant one compared to the other 2 cycles.

4.5.3 Total CO_2 production rate

Figure 4.4 shows the total CO_2 production rate at different total ECs for the three cycles. In this study, the CO_2 production rate was calculated for a total CH_4 and ethanol mineralization (CH_4+ethanol). Over cycles 1 to 3, the mass ratio of P CO_2/EC decreased from 2.2 to 0.5. If CH_4 and ethanol individually are converted to only CO_2 and water (H_2O) through an oxidation reaction in a biofilter, the theoretical mass ratios of P CO_2/EC would be calculated as 2.75 (CH_4) and 1.91 (ethanol) respectively. If biomass production is included (bioxidation), P CO_2/EC will be less than the theoretical values [32].

According to Figure 4.4, during cycle 1, P CO_2/EC of 2.2 exceeded 1.91 (theoretical mass ratio of P CO_2/EC for ethanol mineralization). Therefore, during cycle 1, the CO_2 production was a result of both CH_4 and ethanol mineralization. During cycle 2, P CO_2/EC diminished to 1 which was less than 1.91 and noticeably lower than 2.75. This could be related to the reduced contribution of CH_4 mineralization for CO_2 production comparing with ethanol bioxidation in the biofilter. In other words, competition between CH_4 and ethanol consumption by the microorganisms was probably in the favor of ethanol. In cycle 3, P CO_2/EC dropped to 0.5. According to Figures 4.3 and 4.4, the zero CH_4 elimination at cycle 3 was in the agreement with the low P CO_2/EC of 0.5. During cycle 3, CO_2 was probably produced only by ethanol bioxidation.

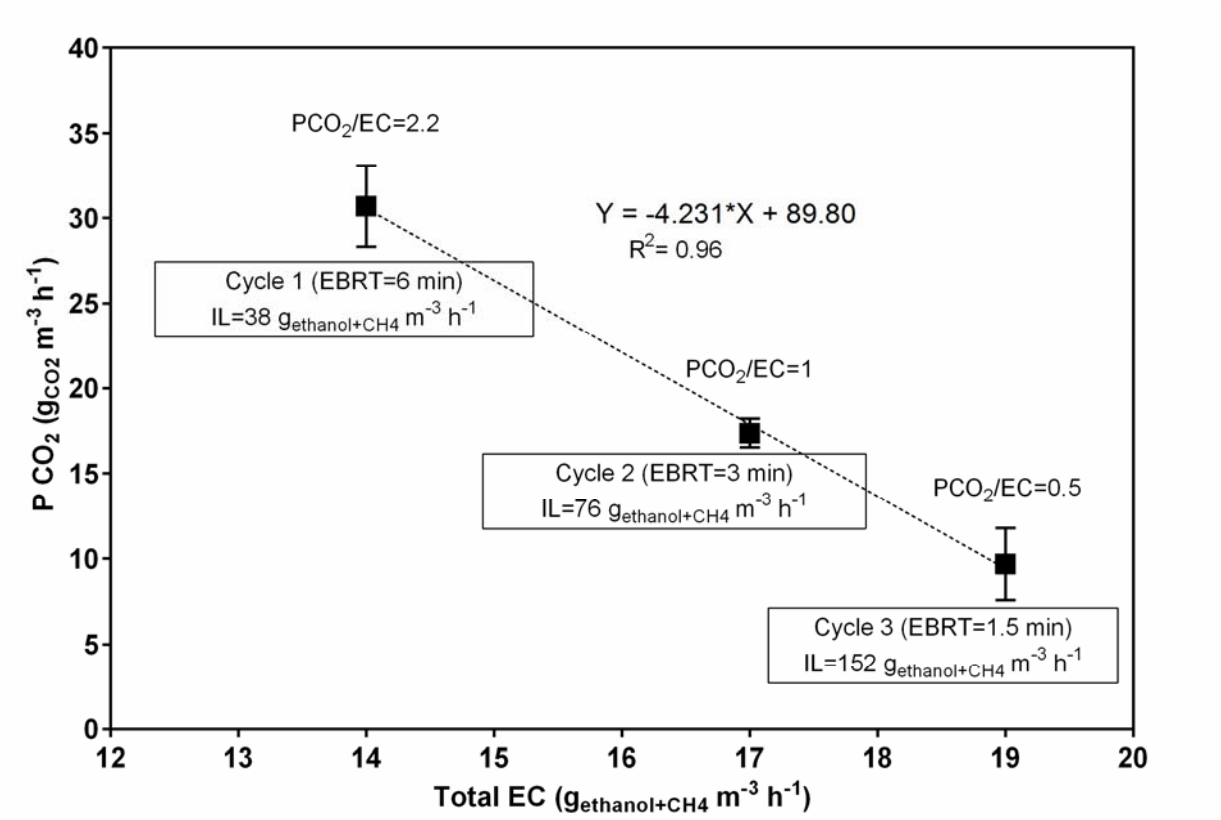

Figure 4.4: Total CO_2 production rate as a function of total EC at different cycles

For CH_4 as a single pollutant, the P CO_2 often followed an increasing trend when the EC increased. For example, Limbri et al. (2014) [33] observed P CO_2 increased from 10 to 40 g_{CO2} m^{-3} h^{-1} when EC increased from 5 to 22 g_{CH4} m^{-3} h^{-1} for a CH_4 IL variation from 17 to 208 g_{CH4} m^{-3} h^{-1} in a biofilter. Figure 4.4 shows that when the total EC increased from 14 to 19 $g_{ethanol+CH4}$ m^{-3} h^{-1}, P CO_2 linearly decreased from 31 to 10 g_{CO2} m^{-3} h^{-1} (R^2 of 0.96) with a negative slope of -4.23. The linear trend of P CO_2 as a function of total EC could mean that the P CO_2 variations over the cycles were proportional to total EC changes. Ménard et al. (2012) [151] observed a linear trend of P CO_2 as a function of total EC variation with a slope of 3 for a biofilter during removal of a mixture of CH_4 and toluene. A linear trend was also observed by Nikiema et al. (2005) [32] for P CO_2s versus ECs (slope =1.6) for CH_4 removal in a biofilter. The negative slope in Figure 4.4 revealed that the substrates (CH_4 or ethanol) were eliminated by conversion to biomass [33] or being dissolved (ethanol) in the leachate [151] as opposed to mineralization.

4.5.4 Methane and ethanol elimination profiles across the filter bed

The CH_4 removal profiles along the filter bed, with and without ethanol, are shown in Figure 4.5 at EBRTs of 6, 3 and 1.5 min corresponding to CH_4 ILs of 33, 66 and 132 $g_{CH4}\ m^{-3}\ h^{-1}$. It should be noted at an EBRT of 1.5 min, no removal (no profile across the filter bed) was observed for CH_4 (CH_4 IL of 136 $g_{CH4}\ m^{-3}\ h^{-1}$) in the presence of ethanol (IL=18 g $m^{-3}\ h^{-1}$). With some exceptions, ethanol was completely eliminated in the biofilter's lowest section (close to the inlet) at ethanol ILs of 4.5, 9 and 18 $g_{ethanol}\ m^{-3}\ h^{-1}$ corresponding to cycles 1, 2 and 3 respectively. According to Figure 4.5, the CH_4 was almost equally removed across the three sections of the biofilter either in the presence or absence of ethanol vapors. Table 4.2 presents a comparison of CH_4 REs with and without ethanol vapors for the different sections of the biofilter for EBRTs of 6 and 3 min. Table 4.2 shows that ethanol addition could drop the CH_4 RE in section 1 as by 33 and 50% under EBRTs of 6 and 3 min respectively when compared to the situation where ethanol is absent.

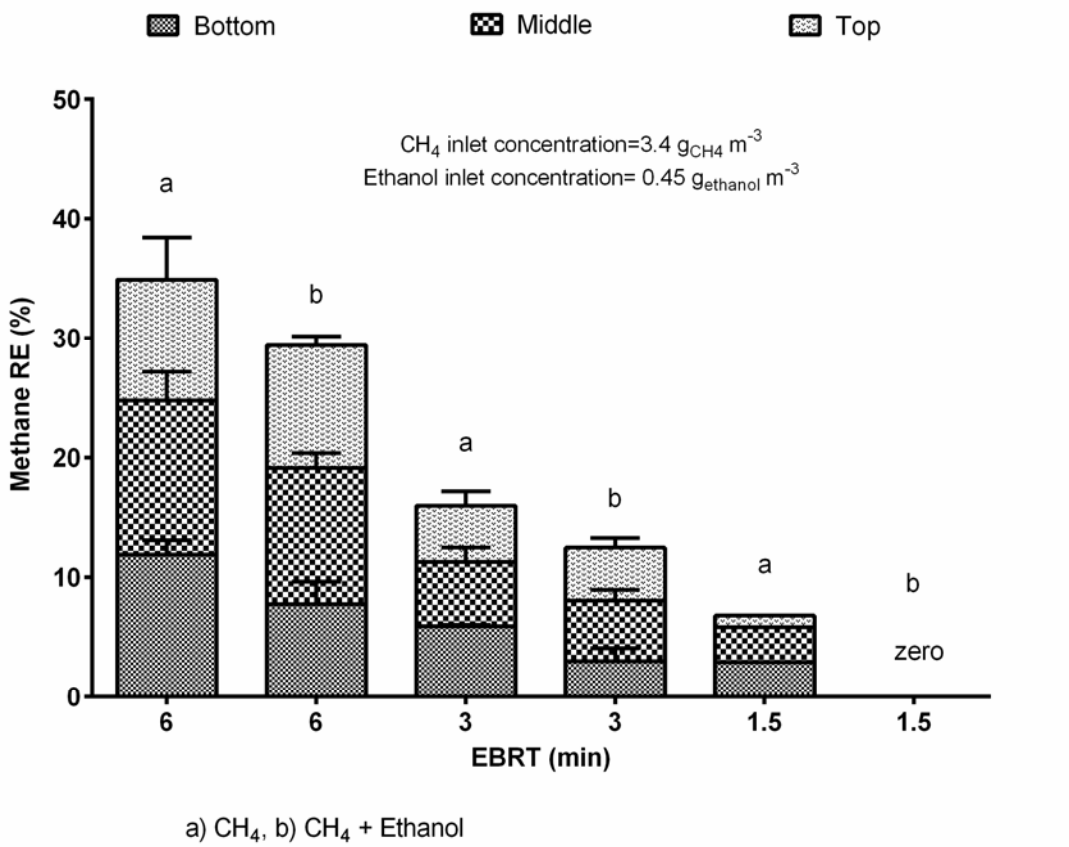

Figure 4.5: Methane elimination profiles across the filter bed at different EBRTs

Because ethanol is completely miscible with water [5], when the EBRT was as long as 6 min, ethanol was mostly absorbed and biodegraded near the inlet of the biofilter and the upper sections were never exposed to ethanol. Nevertheless, at the shorter EBRT of 3 min, a large part of the biofilter was exposed to ethanol. Thus, more methanotrophs could be affected by toxicity or competition for ethanol. According to Table 4.2, the CH_4 REs for the upper sections of the biofilter (middle and top sections) were not affected by ethanol feeding under EBRTs 6 and 3 min.

Table 4.2: Distribution of CH_4 eliminations at different sections of the biofilter

Sections	**Before ethanol addition**		**After ethanol addition**		**CH_4 RE (%) decrease following ethanol addition**	
	CH_4 RE (%)					
	EBRT=6	EBRT=3	EBRT=6	EBRT=3	EBRT=6	EBRT=3
Bottom	12	6	8	3	33	50
Middle	13	5	11	5	1	0
Top	10	6	10	5	0	0

EBRTs are presented in minutes

4.5.5 The biofilter's sensitivity to ethanol additions

Figures 4.6a, b and c display the sensitivity of the biofilter to ethanol addition at cycles 1, 2 and 3 for CH_4 ILs of 33, 66 and 132 g m^{-3} h^{-1} respectively. The recovery of the biofilter after each cycle are also shown in Figure 4.6. According to Figure 4.6a, for an ethanol IL of 4.5 $g_{ethanol}$ m^{-3} h^{-1}, the CH_4 RE suddenly fell down from 35 to 27% for a CH_4 IL of 33 g_{CH4} m^{-3} h^{-1}. Then, CH_4 RE improved and remained almost constant at 29% over cycle 1. The variation of CH_4 RE could be linked to the occasional ethanol inlet concentration fluctuations. When cycle 1 was finished (absence of ethanol) at day 124, the biofilter gradually recovered to the initial CH_4 RE

of 33% in a period of 10 days. In cycle 2 (Figure 4.6b), addition of ethanol with an IL of 9 $g_{ethanol}$ m^{-3} h^{-1} caused the CH_4 RE to drop from 16 to 11% (CH_4 IL of 66 g_{CH4} m^{-3} h^{-1}).

During cycle 2, the CH_4 RE increased from 11 to 14% due to temporary reduction of ethanol inlet concentration form 0.45 to 0.3 $g_{ethanol}$ m^{-3}. The biofilter recovery to the original CH_4 RE of 15% after ethanol was stopped for cycle 2 took 14 days (days 170 to 184).

Figure 4.6c shows that when cycle 3 was started, the CH_4 RE was reduced immediately from 7 to 1% (CH_4 IL of 132 g_{CH4} m^{-3} h^{-1}) as a result of ethanol feeding with an IL of 18 $g_{ethanol}$ m^{-3} h^{-1}.

During cycle 3, no CH_4 elimination was observed. After cycle 3, the CH_4 conversion remained below 1% for the following 7 days (days 253 to 260). Then the CH_4 RE gradually returned to its original value of 7%. The recovery process after cycle 3, was quite slow and took 25 days (days 253 to 278). In general, the recovery time of the biofiler in terms of CH_4 RE was related to EBRT. When EBRT decreased from 6 to 1.5 min, ethanol IL increased from 4.5 to 18 $g_{ethanol}$ m^{-3} h^{-1} and possibly caused more intensive toxic effects on methanotrophs [157]. For the minimum EBRT of 1.5 min, the minimum CH_4 RE of 0% was attained.

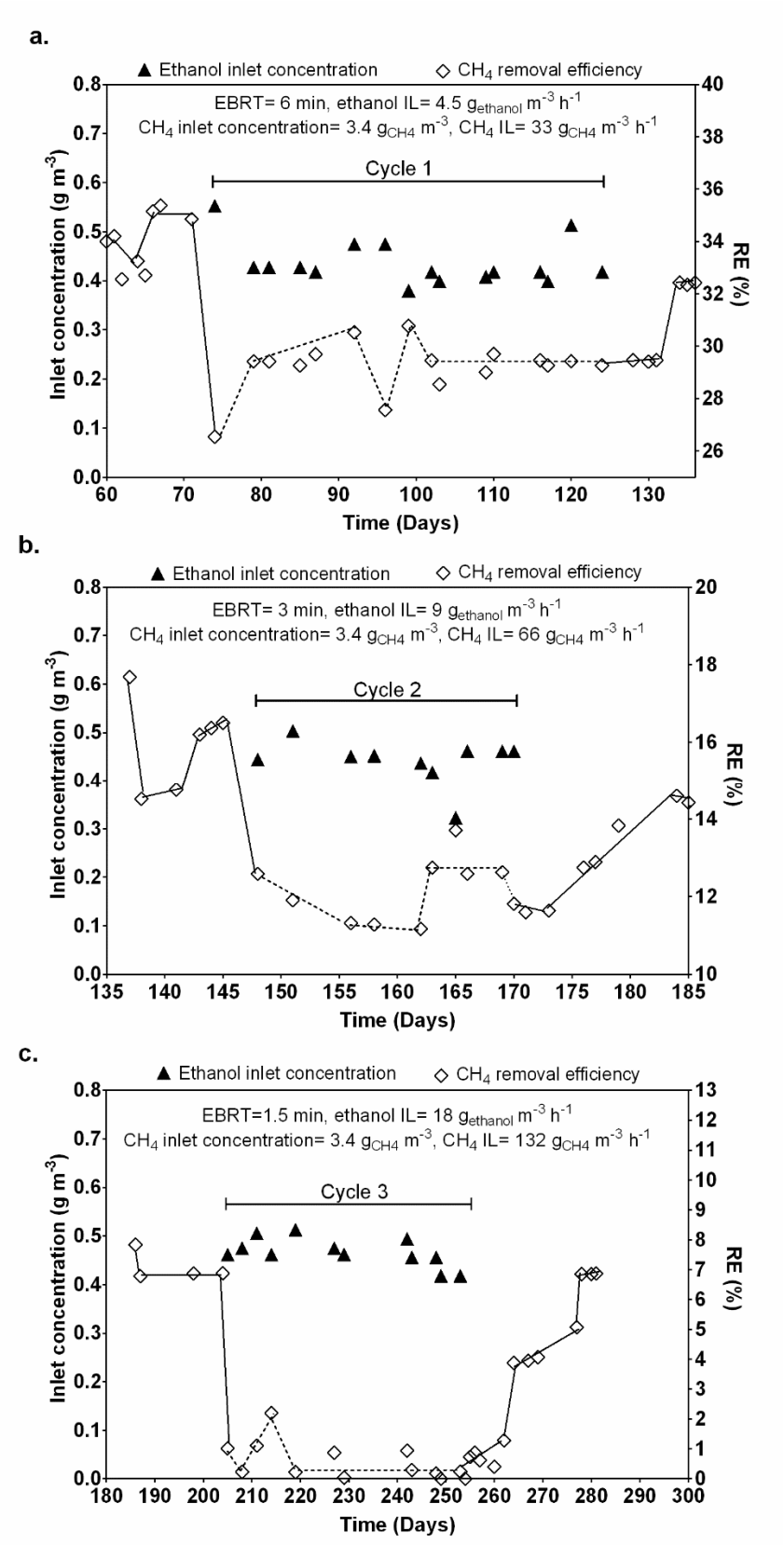

Figure 4.6: The biofilter sensitivity to ethanol additions: a. Cycle 1; b. Cycle 2; C. Cycle 3

4.5.6 The dynamic ethanol concentrations in the leachate

Figures 4.7a, b and c show the dynamic ethanol concentrations in the leachate during cycles 1, 2 and 3 respectively. According to Figure 4.7a, ethanol addition at an IL of 4.5 $g_{ethanol}$ m^{-3} h^{-1} during cycle 1 yielded an average ethanol concentration in the leachate as 1100 ± 200 $g_{ethanol}$ $m^{-3}_{leachate}$. According to Figure 4.7a, ethanol concentration in the leachate generally increased from 850 to 1400 $g_{ethanol}$ $m^{-3}_{leachate}$ until the middle of cycle 1 (days 79 to 102). Then, the ethanol concentration in the leachate declined from 1400 to 1000 $g_{ethanol}$ $m^{-3}_{leachate}$ (days 102 to 120). The ethanol concentration in the leachate was a function of the ethanol concentration in the gas phase. Prior to cycle 1, the biofilm phase was free of ethanol. Over cycle 1, ethanol feeding in the gas phase could build up ethanol in the biofilm phase and consequently in the leachate due to the absorption of ethanol in the biofilm phase. Because, there is almost no limitation for the mass transfer of ethanol from gas to the biofilm phase (dimensionless Henry's law constant of 0.002 at 25 ˚C and 1 atm) [6], ethanol elimination is kinetically limited by bioconversion. Therefore, ethanol concentration in the leachate might gradually increase after a few days. If there was no ethanol conversion, the biofilm phase would be saturated after a short period of time [158]. However, the accumulated ethanol in the biofilm phase was removed through biological conversion. Thereafter, a balance between dissolved, converted and accumulated ethanol was established in the biofilm phase.

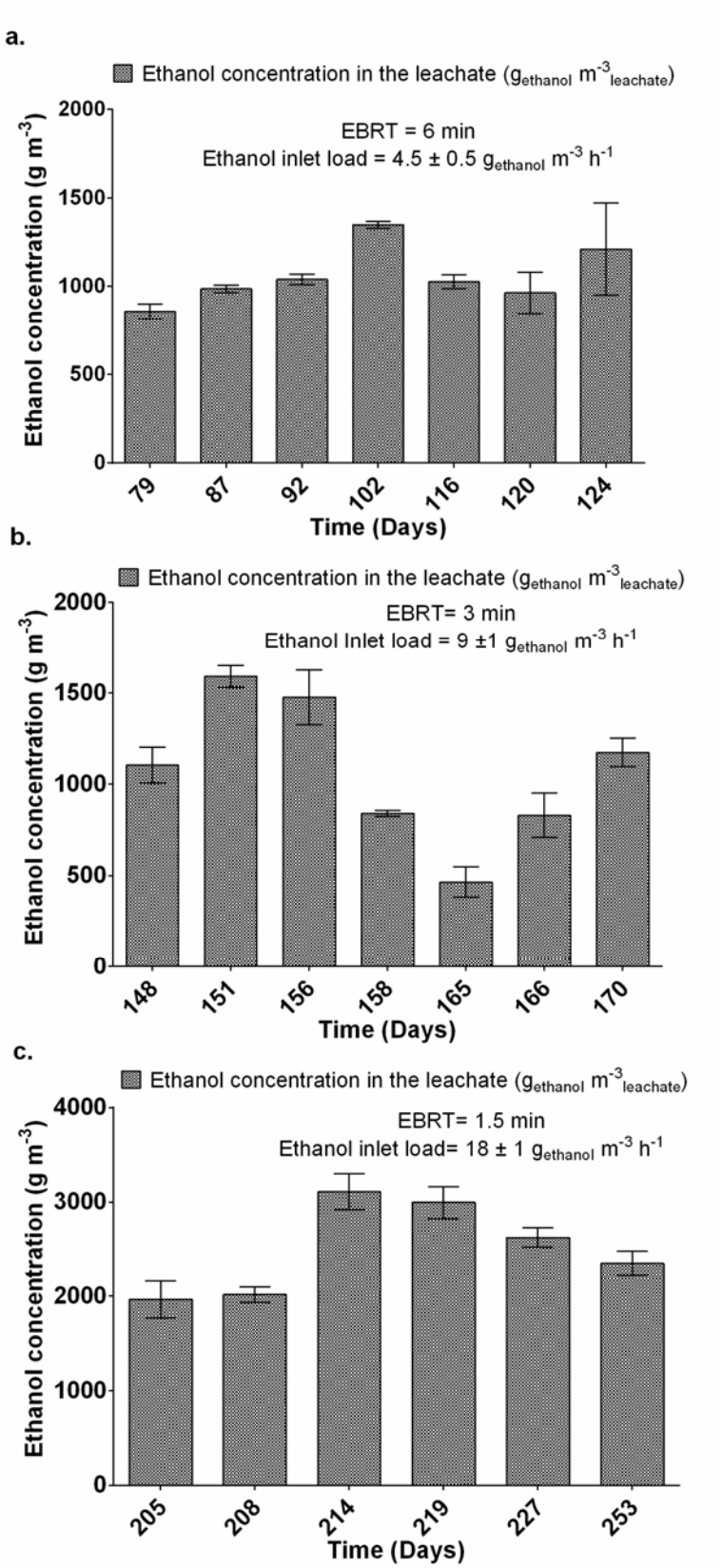

Figure 4.7: Ethanol concentration in the leachate over the time: a. Cycle 1; b. Cycle 2; c. Cycle 3

In addition, before cycle 1, the microbial culture was adapted to CH_4 and there was no ethanol degrading microorganism inoculation to the biofilter. Therefore, probably owing to the lack of appropriate ethanol degrading microorganisms, it took 24 days (days 79 to 102) until the ethanol concentration in the leachate increasing trend stopped. Finally, the ethanol concentration in the leachate temporarily increased again from 1000 to 1200 $g_{ethanol}\ m^{-3}_{leachate}$ from days 120 to 124 due to a corresponding ethanol IL variation from 4.5 to 5 $g_{ethanol}\ m^{-3}\ h^{-1}$. The average ethanol concentration in the leachate during cycle 2 was 1100 ± 350 $g_{ethanol}\ m^{-3}_{leachate}$ for an average ethanol IL of 9 $g_{ethanol}\ m^{-3}\ h^{-1}$. This is similar to the value of cycle 1. Although the ethanol IL (gas phase) during cycle 2 was two fold higher than cycle 1, the biocatalysts for ethanol degrading were more developed and active in cycle 2 compared to cycle 1 and more tolerant to higher ethanol liquid concentrations. Moreover, during cycle 2, ethanol IL occasionally decreased to 6 $g_{ethanol}\ m^{-3}\ h^{-1}$ (days 163 to 165) which caused an ethanol liquid phase concentration reduction to 500 $g_{ethanol}\ m^{-3}_{leachate}$ (Figure 4.7b).

During cycle 3, the average ethanol concentration in the leachate reached 2500 ± 400 $g_{ethanol}\ m^{-3}_{leachate}$ which was a significant increase compared to cycles 1 and 2. As a result of ethanol kinetic limitations, higher ethanol ILs during cycle 3 compared to cycles 1 and 2, resulted in higher ethanol concentrations in the biofilm phase. Morotti et al. (2011) [55] obtained an ethanol concentration in the leachate as 1000 $g_{ethanol}\ m^{-3}_{leachate}$ for an ethanol IL of 25 $g_{ethanol}\ m^{-3}\ h^{-1}$ in a clay ball biofilter. This is almost half of the ethanol concentration in the leachate at cycle 3 in the current study. The difference can be attributed to the ethanol RE of 90% reported by Morotti et al. (2011) [55] for an ethanol IL of 25 $g_{ethanol}\ m^{-3}\ h^{-1}$. Nevertheless, in the present study, complete removal of ethanol in the case of either biodegradation or absorption was obtained in cycle 3 for an ethanol IL of 18 $g\ m^{-3}\ h^{-1}$.

4.5.7 The dynamic leachate clean up after ethanol vapor termination

The ethanol concentration in the leachate was in equilibrium with the ethanol concentration in the gas phase [18]. Therefore, when the ethanol vapor addition was finished at the end of each cycle, the leachate should have been free of ethanol. When cycles 1 and 2 were finished, the leachate clean-up was immediate such that one day after the cycles, the ethanol concentrations in the leachate were almost zero. However, after cycle 3, the leachate clean-up was delayed for 6 days. Figure 4.8 shows the leachate clean up over the time after cycle 3. One day after cycle

3 ended (day 254) the ethanol concentration in the leachate was still 1250 $g_{ethanol}$ $m^{-3}_{leachate}$. However, over the time, the ethanol concentration in the leachate gradually decreased from 1250 to 200 $g_{ethanol}$ $m^{-3}_{leachate}$. The presence of ethanol in the leachate for a few days after cycle 3's end can be explained by an exceeding accumulation of ethanol in the biofilm phase during cycle 3 compared to cycles 1 and 2. In other words, an ethanol IL of 18 $g_{ethanol}$ m^{-3} h^{-1} favored excess amount of ethanol in the biofilm phase rather than 4.5 and 9 $g_{ethanol}$ m^{-3} h^{-1} during cycles 1 and 2 respectively. Therefore, a longer time (6 days) was needed for the accumulated ethanol to be removed from the biofilm phase compared to 1 day for cycles 1 and 2.

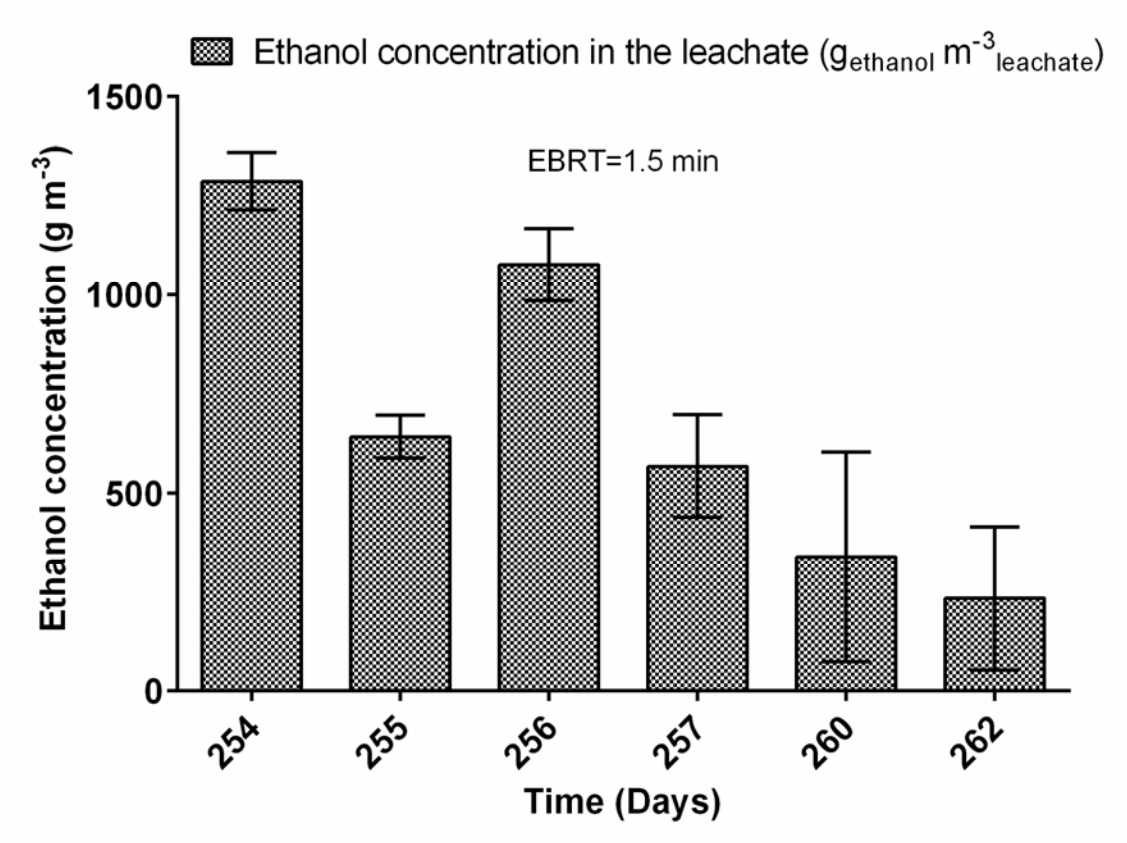

Figure 4.8: Leachate clean up over the time after cycle 3

4.6 Conclusion

The inorganic bed biofilter operated during 281 days in order to eliminate CH_4 and a mixture of CH_4 and ethanol. Ethanol additions were performed over three cycles based on gas flow rate stepwise variation as 3, 6 and 12 L min^{-1} corresponding to EBRTs of 6, 3 and 1.5 min. The gas

flow rate variations from 3 to 12 L min^{-1} as well as ethanol additions could separately influence the CH_4 RE in the biofilter. The CH_4 RE declined from 35 to 7% as a result of CH_4 IL variations from 33 to 132 g_{CH4} m^{-3} h^{-1} due to gas flow rate variations from 3 to 12 L min^{-1}. Moreover, the presence of ethanol resulted in a CH_4 RE decrease up to 100% of its original value (from 7 to 0%) when the gas flow rate was at the maximum value of 12 L min^{-1} (EBRT of 1.5 min). However, neither the ethanol IL variations from 4.5 to 18 $g_{ethanol}$ m^{-3} h^{-1} with the gas flow rate variation nor the presence of CH_4 influenced the complete removal of ethanol during the biofilter's operation. As a result, when both CH_4 and ethanol were present, the optimum operation condition to obtain maximum elimination of CH_4 (RE_{CH4}=35%) was the minimum gas flow rate of 3 L min^{-1} (EBRT of 6 min) corresponding to CH_4 IL and ethanol IL of 33 g_{CH4} m^{-3} $h^{-1}$and 4.5 $g_{ethanol}$ m^{-3} h^{-1}. Ethanol was observed in the leachate in concentrations ranging from 850 to 2500 $g_{ethanol}$ $m^{-3}_{leachate}$ which corresponded to ethanol accumulation in the biofilm phase. In addition, the periodic ethanol addition provided a better understanding of the biofilter dynamic behaviors during the cycles and the biofilter's resumption after each cycle. After cycles 1 and 2, the biofilter could return to original the CH_4 REs in a few days. The biofilter recovery period after the ends of cycles 1, 2 and 3 were 10, 14 and 25 days respectively. When cycle 3 ended, ethanol was still present in the leachate with a concentration of 1250 $g_{ethanol}$ $m^{-3}_{leachate}$.Therefore, the presence of ethanol in the biofilm phase was thought to delay the return to normal performance of the biofilter in terms of CH_4 RE after cycle 3.

4.7 Acknowledgments

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CHAPTER 5. Methane biofiltration in the presence of ethanol vapor under steady and transient state conditions: An experimental study

Avant propos:

L'article "Methane biofiltration in the presence of ethanol vapor under steady and transient state conditions: An experimental study*"* a été soumis au journal "*Environmental Science and Pollution Research*" en décembre 2016.

TITRE: Biofiltration du méthane en présence d'éthanol en régimes permanent et transitoire: une étude expérimentale

Title: Methane biofiltration in the presence of ethanol vapor under steady and transient state conditions: An experimental study

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Contribution to the document: This paper is relevant to the third objective of the thesis. Two CH_4 biofilters with different packing materials in their bottom sections in the absence and presence of ethanol were evaluated and compared. Both biofilters were operated under different transient conditions (e.g., ethanol shock load, starvation) and their performance were compared and discussed.

Methane biofiltration in the presence of ethanol vapor under steady and transient state conditions: An experimental study

5.1 Résumé

L'élimination du méthane (CH_4) par biofiltration en présence d'éthanol a été étudiée en parallèle sur un lit de pierre et sur un garnissage mixte. Le biofiltre ayant un garnissage mixte était constitué de pierres (occupant les 2 sections supérieures du biofiltre) et de matériau inorganique (occupant la section inférieure du biofiltre). L'utilisation de divers garnissages dans les sections inférieures des biofiltres découle du fait que cette partie du biofiltre joue un rôle prépondérant lors de l'élimination du CH_4 et de l'éthanol. Les conversions du CH_4 et de l'éthanol de même que la production de dioxyde de carbone (CO_2) ainsi que la perte de charge ont été étudiées sur diverses sections du biofiltre. Une conversion de CH_4 de 55 ±1% a été obtenue pour les 2 biofiltres sous des charges à l'entrée de 13 ±0.5 g_{CH4} m^{-3} h^{-1} et un temps de résidence en fût vide de 6 min en régime permanent. L'ajout progressif d'éthanol en 4 phases de 1 à 11 $g_{éthanol}$ m^{-3} h^{-1} a diminué la conversion du CH_4 dans les sections inférieures des biofiltres de 14 à 9 % et de 15 à 5% pour le biofiltre à base de pierres et le biofiltre mixte. Il est à noter que l'éthanol est éliminé complétement dans les sections inférieures des biofiltres pour des charges d'éthanol variant entre 1 et 11 $g_{éthanol}$ m^{-3} h^{-1} et produit du CO_2 (14 g_{CO2} m^{-3} h^{-1} dans la section inférieure du biofiltre à base de pierres et 11 g_{CO2} m^{-3} h^{-1} dans la section inférieure du biofiltre mixte). Les 2 biofiltres répondent rapidement à une variation par à-coups d'éthanol suivie d'une carence et une baisse de 20 % de la conversion est notée. Suite au régime transitoire, la récupération des 2 biofiltres a pris moins de 5 jours. Contrairement au biofiltre mixte, la perte de charge (pouvant atteindre 1.9 cm H_2O m^{-1}) était une contrainte importante pour le biofiltre à base de pierres. L'accumulation de biomasse dans la partie inférieure du biofiltre à base de pierres contribue pour 50 % la perte de charge totale. Cependant, une carence menée sur 14 jours réduit la perte de charge à 0.25 cm H_2O m^{-1}.

Mots-clefs : Méthane, biofiltre, éthanol, garnissage, mixte, transitoire

5.2 Abstract

Methane (CH_4) removal in the presence of ethanol vapors was performed by a stone-based bed and a hybrid packing biofilter in parallel. In the absence of ethanol, a methane removal efficiency of 55 ±1% was obtained for both biofilters under similar CH_4 IL of 13 ±0.5 g_{CH4} m^{-3} h^{-1} and an empty bed residence time (EBRT) of 6 min. The results proved the key role of the bottom section in both biofilters for simultaneous removal of CH_4 and ethanol. Ethanol vapor was completely eliminated in the bottom sections for an ethanol IL variation between 1 to 11 $g_{ethanol}$ m^{-3} h^{-1}. Ethanol absorption and accumulation in the biofilm phase as well as ethanol conversion to CO_2 contributed to ethanol removal efficiency of 100%. In the presence of ethanol vapor, CO_2 productions in the bottom section increased almost 4-fold in both biofilters. The ethanol concentration in the leachate of the biofilter exceeding 2200 $g_{ethanol}$ $m^{-3}_{leachate}$ in both biofilters demonstrated the excess accumulation of ethanol in the biofilm phase. The biofilters responded quickly to an ethanol shock load followed by a starvation with 20% decrease of their performance. The resumption of both biofilters after the transient conditions took less than 5 days. Unlike the hybrid packing biofilter, excess pressure drop (up to 1.9 cmH_2O m^{-1}) was an important concern for the stone bed biofilter. The biomass accumulation in the bottom section of the stone bed biofilter contributed to 80% of the total pressure drop. However, the 14-day starvation reduced the pressure drop to 0.25 cmH_2O m^{-1}.

Keywords: Methane, biofiltration, ethanol, packing material, hybrid biofilter, transient state

5.3 Introduction

Methane (CH_4) has hazardous environmental impacts in terms of climate change and global warming [159]. Presently, CH_4 is the second most abundant greenhouse gas (GHG) after carbon dioxide (CO_2) worldwide [35]. Globally, 16% of GHG emissions belong to CH_4 emissions which are two and a half times higher than the pre-industrial levels [154]. The global warming potential (GWP) of CH_4 (over 100 years period) is estimated to be 28-36 times higher than CO_2 [2]. Methane can be produced by manmade activities such as anaerobic digestion processes in wastewater treatment plants (WWTPs) [160, 161]. Ethanol is widely used at ethanol refineries, food and beverage industries. In the United States, 5% of total CH_4 emissions are produced in WWTPs related to ethanol industries [2]. As a result, the waste gas treatment unit in ethanol plants can receive ethanol vapors and CH_4 simultaneously.

Biofiltration has been suggested as a promising technique in order to reduce anthropogenic CH_4 emissions with concentrations lower than 10 $g_{CH4}\ m^{-3}$ [162]. In biofiltration, CH_4 is converted to CO_2, water, biomass and etc. by CH_4 degrading bacteria (e.g., methanotrophic bacteria) during the passage of a polluted and humid air stream through a packed column [13]. According to the presence of a gas phase and a biofilm phase in contact with each other, CH_4 biofiltration is limited by CH_4 mass transfer from gas to the biofilm phase [8]. The CH_4 mass transfer limitation is related to CH_4 low water solubility [155] (dimensionless Henry's law constant of 28 at 25 ˚C and 1 atm [6]). The implementation of high surface area particles (>1000 $m^2\ m^{-3}$) as filter bed could overcome the CH_4 mass transfer limitations in a biofilter [77]. In addition, empty bed residence time (EBRT) for CH_4 biofilters is usually longer than 4 minutes in order to increase CH_4 mass transfer from gas to the biofilm phase [111].

Nevertheless, the appropriate operating conditions such as packing materials or EBRT for alcohol vapors removal in biofilters are different compared to CH_4. Low ethanol dimensionless Henry's constant (0.002 at 25 ˚C and 1 atm) [5], represents less limitations for ethanol mass transfer from gas to the biofilm phase. Therefore, ethanol biofilters are usually operated under EBRTs less than 1 min [107]. Filter bed is also a key parameter for ethanol biofilters in terms of excess pressure drop. Exceeded solubility of ethanol in the biofilm phase may result in excess biomass production [163]. Thus, the biomass accumulated occupies the void spaces between the packing materials and leads to increased pressure drop in an ethanol biofilter [85].

Therefore, the elimination of CH_4 and ethanol vapors in a mixture by biofilters can produce a combination of limitations with respect to each pollutant. The type of packing materials as well as EBRT are likely two important limiting factors when CH_4 and ethanol vapors are present in a mixture in a biofilter.

According to the industrial applications of biofilters for CH_4 and ethanol vapors in a mixture, a departure from steady state conditions is possible as a result of shock loads or shutdowns [56]. For example, at ethanol industries, an abrupt variation of ethanol emissions from a specific unit may apply a sudden change to the biofilter. In addition, temporary shutdowns can happen for biofilters during holidays or maintenance periods and cause starvation conditions. The dynamic behavior of biofilters during shock loads or starvation conditions should be studied for certain industries in order to evaluate the stability of the biocatalysts. Moreover, the biofilter evaluations

during transient loadings provide a better understanding of the biofiltration process and the associated phenomena. To our knowledge, no investigation has been performed on the CH_4 and ethanol biofiltration in a mixture neither under steady state nor transient state conditions.

The aim of the present study was to compare the performance of a stone-based bed biofilter (SBF) and a hybrid bed biofilter (HBF) (stone and inorganic balls) for different mass ratio of ethanol/CH_4 under steady state and transient conditions. Under steady state condition, the performance of the SBF and HBF were evaluated and compared during the absence of ethanol as well as during stepwise increase of ethanol inlet concentration. The transient behavior of SBF and HBF were studied and compared by sudden ethanol inlet concentration variations for a few days. Finally, a shutdown was applied to the SBF and HBF in order to study the biofilter behavior during and after starvation period.

5.4 Materials and methods

5.4.1 Experimental setup

Figure 5.1 shows the experimental setup. Two identical biofilters were used in parallel. Each biofilter was made of three equal size Plexiglas tubes. The diameter and length of the tubes were 0.15 and 0.33 m respectively. The total height and total volume of both biofilters were 1 m and $18*10^{-3}$ m^3 respectively. The stone bed biofilter (SBF), was packed by identical packing materials in each of its three sections whereas the hybrid packing biofilter (HBF) had two types of packing materials. The bottom section of the HBF was packed with inorganic balls while the middle and top sections were packed with the same stones (gravels) as SBF. Both packing materials (stones and inorganic balls) were selected as inert materials. Both of the packing materials used in this study were non-biodegradable and non-compactible.

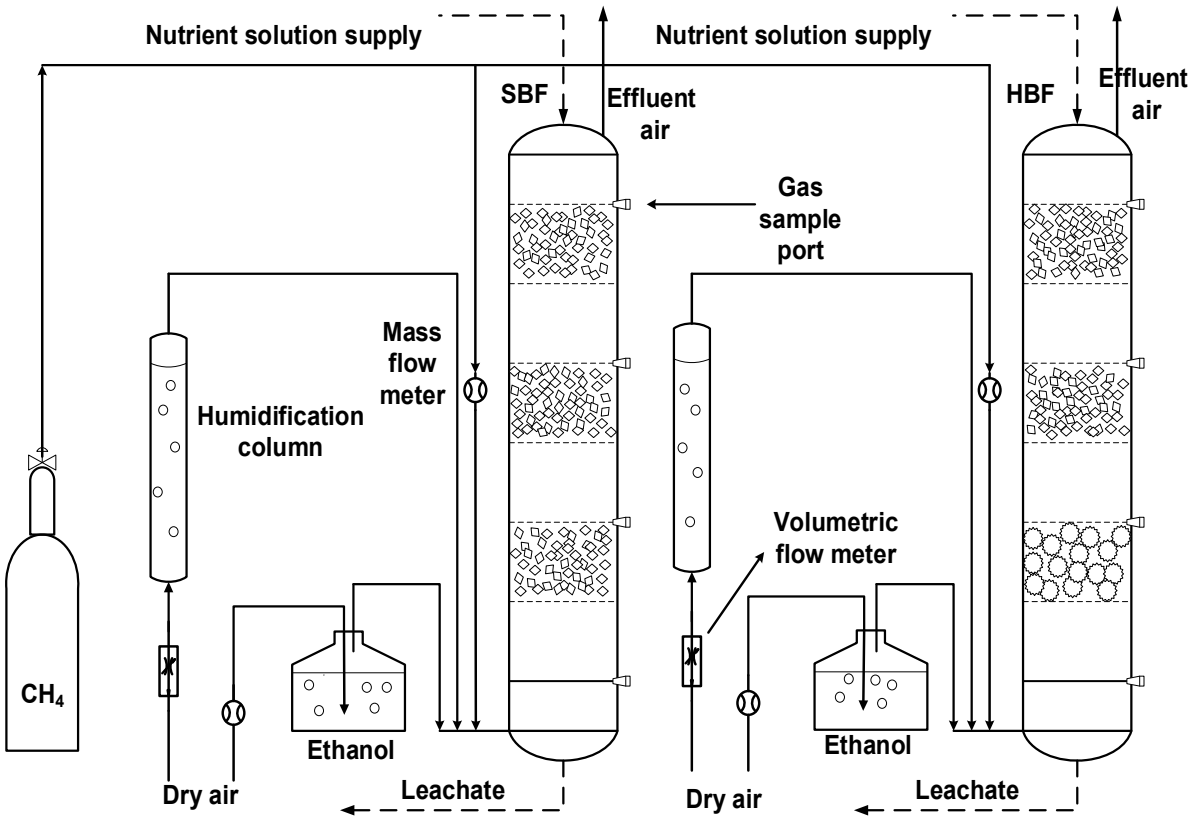

Figure 5.1: The schematic of the biofilters

The characteristics of both packing materials are summarized in Table 5.1. The exact name of the packing materials cannot be disclosed according to a confidential agreement. Four gas sampling ports were located along each biofilter in order to collect CH_4, ethanol and CO_2 from the inlet, bottom, middle and top sections. A nutrient solution with sources of nitrogen, phosphorous, copper and potassium were fed daily to SBF and HBF separately at a rate of 1 L min^{-1} during 1 min. The nutrient solution composition was the same used by Ménard et al. (2012) [151]. The CH_4 was supplied from a CH_4 cylinder (Praxair Inc. (Sherbrooke, Canada) with a purity of 99% (v/v) and a regulated pressure. In order to make an appropriate CH_4 inlet concentration, the CH_4 stream provided from the CH_4 cylinder was diluted by air. The CH_4 flow rate and air stream were controlled by mass flow meters (Brooks Series 8800) respectively. The humid air was generated from a humidification column. Ethanol was produced by passing air

through an ethanol bubbler. Methane, ethanol vapors and humid air were mixed and sent to the bottom of the biofilters in order to provide an upward flow.

Table 5.1: Characteristics of the packing materials

Packing material	Average diameter (m)	Specific surface area ($m^2\ m^{-3}$)	Void space (%)	Reference
Stone	$(7\pm1)*10^{-3}$	470	43	[150]
Inorganic ball	$(12\pm4)*10^{-3}$	310	40	[164]

5.4.2 Microbial culture and inoculation

First, 10 L of tap water was fed to the SBF and HBF separately in order to moisten the packing materials. Accordingly, a leachate from an active CH_4 biofilter [56] was used to inoculate both SBF and HBF. Four liters of the leachate were taken from the CH_4 biofilter and fed to the top of SBF or HBF. Finally, the leachate was recycled 4 times for each biofilter.

5.4.3 Analytical methods

A total hydrocarbon analyzer (FIA 510, Horiba, USA) was used for measuring the individual concentrations of CH_4 and ethanol. When both pollutants were present in a mixture, the total concentration was measured. Then, the CH_4 inlet stream was temporarily cut from the biofilter. The CH_4 concentration was calculated based on the difference between the total and the ethanol concentrations. A CO_2 gas analyzer (Ultramat 22P, Siemens, Germany) was used in order to determine the CO_2 concentrations. The dissolved ethanol in the leachate was analyzed by a total organic carbon analyzer (TOC-V_E, Shimadzu, Japan). The filter bed pressure drop was measured by a differential manometer (Type 4, Air Flow Developments Ltd., UK).

5.4.4 Performance parameters

The following equations present the parameters describing the performance of the biofilters.

Removal efficiency (RE)	$\frac{(C_{Gi} - C_{Go})}{C_{Gi}} \times 100$	(%)
Elimination capacity (EC)	$\frac{(C_{Gi} - C_{Go}) \times Q}{V_{bf}}$	(g m^{-3} h^{-1})
Inlet load (IL)	$\frac{Q \times C_{Gi}}{V_{bf}}$	(g m^{-3} h^{-1})
CO_2 production rate (P_{CO_2})	$\frac{(CO_{2_{Out}} - CO_{2_{in}}) \times Q}{V_{bf}}$	(g m^{-3} h^{-1})

In the equations above, the inlet and outlet pollutants concentrations were defined by C_{Gi} and C_{Go} respectively ($g_{CH_4} m^{-3}$ or $g_{ethanol}\, m^{-3}$). The inlet and outlet CO_2 concentrations were $CO_{2_{in}}$ and $CO_{2_{Out}}$ ($g_{CO_2} m^{-3}$) respectively. The symbols of V_{bf} and Q stand for the biofilter volume (m^3) and the gas flow rate (m^3 h^{-1}) respectively.

5.4.5 The experimental methods

Both biofilters (SBF and HBF) worked under similar operating conditions in terms of gas flow rate, CH_4 and ethanol ILs. The steady state experiments were carried out over 5 phases based on the ethanol/CH_4 mass ratio variations from 0 to 0.8 $g_{ethanol}$ /g_{CH4}. The gas flow rates were fixed at 3 L min^{-1} to provide an empty bed residence time (EBRT) of 6 min for the biofilters during Phases 1 to 5. Methane ILs were constant at 13 ±0.5 g_{CH4} m^{-3} h^{-1} over Phases 1 to 5. At Phase 1, the biofilters were fed with only CH_4. In order to have a better acclimation, the biofilters were operated under CH_4 ILs of 3 ±0.5 g_{CH4} m^{-3} h^{-1} during the first two days of Phase 1 [99]. Ethanol ILs varied stepwise in the range of 0 to 11 ±0.5 $g_{ethanol}$ m^{-3} h^{-1} from Phases 1 to 5. The steady state performance of the SBF and HBF were evaluated in terms of CH_4 and ethanol REs, ECs, PCO_2s, ethanol concentration in the leachate of biofilters and pressure drop over the phases. The transient state experiments were conducted by a shock load followed by a starvation period for the SBF and HBF. In both biofilters, the ethanol IL suddenly increased to almost 5 times its original value from 11 ±0.5 to 53 ±0.5 $g_{ethanol}$ m^{-3} h^{-1} for 4 days and the dynamic behavior of the biofilters was studied in terms of REs, PCO_2s and ethanol concentrations in the leachate. During the shock loads, the CH_4 IL and gas flow rate were kept constant at 13 ±0.5 g_{CH4} m^{-3} h^{-1} and 3 L min^{-1} respectively. After the shock loads, ethanol IL was brought back to

its original value of 11 ±0.5 $g_{ethanol}$ m^{-3} h^{-1} and subsequently, the resumptions of the biofilters were evaluated during 4 days. The following starvation periods were performed by the absence of CH_4, ethanol and nutrient solution during 14 days. During the starvation period, the biofilters were only fed with humid air streams with corresponding gas flow rates of 3 L min^{-1}. After the starvation period, the recovery of the biofilters was examined for the following 5 days. Table 5.2 summarizes the operating conditions of the biofilters under steady state and transient state experiments.

Table 5.2: Experimental conditions for SBF and HBF

Experiments	**Phases**	**Time (days)**	**Gas flow rate (L min^{-1})**	**Methane IL (g m^{-3} h^{-1})**	**Ethanol IL (g m^{-3} h^{-1})**
Startup	-	2	3	3	0
Acclimation	-	3-36	3	13	0
Steady state	1	37-46	3	13	0
	2	47-60	3	13	1
	3	61-74	3	13	3
	4	75-88	3	13	6
	5	89-102	3	13	11
Transient state	Shock load (Phase a)	103-106	3	13	53
	Recovery (Phase b)	107-110	3	13	11
	Starvation (Phase c)	111-124	0	0	0
	Recovery (Phase d)	125-129	3	13	11

5.5 Results and discussions

5.5.1 The overall performance of the SBF and HBF under steady state conditions

Figures 5.2a and b show the overall performance of the SBF and HBF respectively during the 5 phases. During the startup period (2 days) both biofilters reached REs exceeding 20% for corresponding CH_4 ILs of 3 ±0.5 g_{CH4} m^{-3} h^{-1} in 2 days. For the following 27 days (acclimation period), both biofilters operated under a CH_4 IL of 13 ±0.5 g_{CH4} m^{-3} h^{-1} to ensure the microbial culture developed and stabilized. During the acclimation period, the CH_4 REs increased rapidly from 40 to 85% and from 40 to 68% for the SBF and HBF respectively during the first 10 days. Then, the CH_4 REs gradually decreased from 85 to 48% and from 68 to 63% until the end of acclimation period (day 36). The increasing-decreasing pattern of RE in a CH_4 biofilter could be attributed to a methanotrophs population level peak during the first weeks (2-3 weeks) [165]. Kim et al. (2014) [165] observed a similar pattern in terms of CH_4 RE during a 68-day acclimation period. The CH_4 RE increased rapidly from 0 to 54% for a CH_4 IL of 100 g m^{-3} h^{-1} during 21 days, then declined to 33% for the rest of the acclimation period. During Phase 1 (np ethanol addition), both biofilters exhibited a stable condition with an average CH_4 RE of 55 ±1% and a CH_4 EC of 7 ±0.5 g m^{-3} h^{-1} for a corresponding CH_4 IL of 13 ±0.5 g_{CH4} m^{-3} h^{-1}. Table 5.3 shows some recent studies on CH_4 biofiltration. According to Table 5.3, CH_4 REs were in the range of 20 to 60% for CH_4 ILs ranging from 20 to 135 g_{CH4} m^{-3} h^{-1}. In the present study, both biofilters showed a promising performance for CH_4 removal. According to Figures 5.2a and b, ethanol addition to the SBF and HBF over Phases 2 to 5 with an ethanol IL stepwise variations from 1 to 11 g m^{-3} h^{-1} dropped CH_4 REs from 55 ±1% to 43 ±1% for SBF and from 55 ±1% to 46% ±1% for HBF. The corresponding CH_4 ECs decreased from 7 to 5.5 g_{CH4} m^{-3} h^{-1} and from 7 to 6.5 g_{CH4} m^{-3} h^{-1} for SBF and HBF respectively. The toxic effect of ethanol for methanotrophs could reduce the CH_4 RE and EC for both biofilters [157]. For SBF, the stepwise ethanol addition (Phases 2 to 5) with corresponding ILs of 1, 3, 6 and 11 ±0.5 $g_{ethanol}$ m^{-3} h^{-1} ended up to CH_4 REs of 53 ±2%, 47 ±2%, 44 ±2% and 43 ±1% respectively over Phases 2 to 5 for a CH_4 IL of 13 ±0.5 g m^{-3} h^{-1} (Figure 5.2a). For HBF, the presence of ethanol vapors with corresponding ethanol ILs of 1, 3, 6 and 11 ±0.5 $g_{ethanol}$ m^{-3} h^{-1} resulted in respective CH_4 REs of 56 ±3%, 44 ±2%, 46 ±3%, 46 ±1% for a CH_4 IL of 13 ±0.5 g m^{-3} h^{-1} over Phases 2 to 5 (Figure 5.2b).

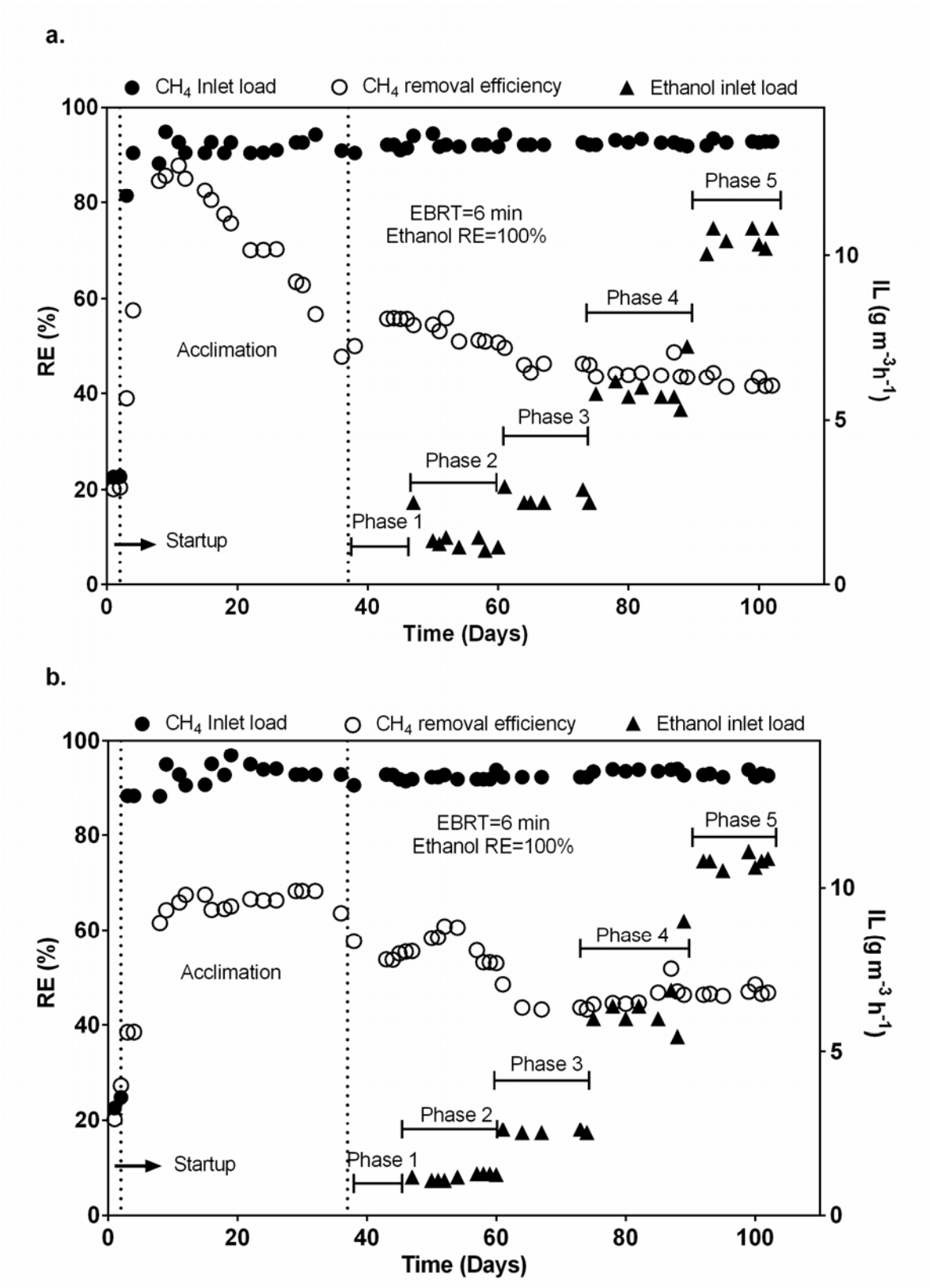

Figure 5.2: The overall performance of the biofilters as a function of time. a. SBF, b. HBF

Ethanol was completely removed (ethanol RE of 100%) either in the SBF or HBF during Phases 2 to 5 for ethanol IL variations from 1 to 11 ±0.5 $g_{ethanol}$ m^{-3} h^{-1}. Ethanol could have been readily absorbed in the biofilm phase of either SBF or HBF because of its complete miscibility with water and its low Henry's constant. Equations (1) and (2) show the biodegradation mechanism of CH_4 and ethanol (C_2H_5OH) to CO_2 respectively and the associated intermediates [13, 55].

$$CH_4 \longrightarrow CH_3OH \longrightarrow CH_2O \longrightarrow HCOOH \longrightarrow CO_2 \quad (1)$$

$$C_2H_5OH \longrightarrow CH_3COH \longrightarrow CH_3COOC_2H_5 \longrightarrow CO_2 \quad (2)$$

According to Eq. (1), CH_4 is transformed to methanol (CH_3OH), formaldehyde (CH_2O) and formic acid (HCOOH) in order to be converted to CO_2. Ethanol bioxidation to CO_2 occurs through respective intermediate compounds such as acetaldehyde (CH_3COH), acetic acid (CH_3COOH) and ethyl acetate ($CH_3COOC_2H_5$) (Eq. (2)).

Table 5.3: Recent studies on CH_4 biofiltration

Filter bed	IL (g_{CH4} m^{-3} h^{-1})	EBRT (min)	RE (%)	Reference
Expanded vermiculite	20	7	30	[4]
Stone + activated carbon	30	20	60	[166]
Coal	135	3	20	[33]
(Wood chips+ perlite+ compost)	20	4	60	[155]
Concrete	40	1	30	[111]
SBF	13	6	67	Present study
HBF	13	6	60	Present study

5.5.2 Methane removal and Carbon dioxide production rate profiles across SBF and HBF

Overall performance parameters (e.g., total RE, EC, P_{CO_2}) provide general information about the behavior of a biofilter. While CH_4 and ethanol are present in a mixture, most of the ethanol is likely to be absorbed and eliminated at the lowest section of the biofilter whereas CH_4 should be eliminated in every biofilter section. In addition, the bottom section packing materials for both biofilters were different. Thus, in the present study, the performance of the biofilters in

terms of RE and P_{CO_2} in each of the three sections should be compared. Figures 5.3a and b show the CH_4 RE profiles for SBF and HBF respectively over phases 1 to 5 as a function of ethanol IL. According to Figures 5.3a and b, the addition of ethanol with corresponding IL variations from 1 to 11 g m^{-3} h^{-1} (Phase 2 to 5) decreased the bottom section CH_4 REs from 14 to 9% and from 15 to 5% for the SBF and HBF respectively. Less than 25% of the CH_4 removal was obtained in the bottom section of both biofilters in the absence of ethanol (Phase 1). In the presence of ethanol (Phases 2 to 5), the bottom section contribution for CH_4 elimination (RE in the bottom section divided by total RE) reduced from 25% to 20% and from 25% to 10% for the SBF and HBF respectively. On the other hand, ethanol was completely removed in the bottom sections of both biofilters. The complete ethanol removal in the bottom sections of both biofilters in the present study could be attributed to the long EBRT (6 min). In this case, the EBRT was adequate such that the ethanol primary absorbed in the biofilm phase of both bioflters lowest section and gradually degraded. Morotti et al. (2011) [55] also observed a high ethanol removal (80%) in the bottom section of a biofilter for an IL of 27 g m^{-3} h^{-1} (ethanol inlet concentration of 0.5 $g_{ethanol}$ m^{-3}, EBRT of 1 min).

Figures 5.4a and b show the P_{CO_2} profile for SBF and HBF respectively across the biofilters within Phases 1 to 5. According to Figures 5.4a and b, when the ethanol IL varied from 0 to 11±0.5 $g_{ethanol}$ m^{-3} h^{-1}, for a constant CH_4 IL of 13 ±0.5 g m^{-3} h^{-1}, the P_{CO_2}s of the SBF and HBF bottom sections increased from 4 ±1 to 18 ±2 g_{CO2} m^{-3} h^{-1} (350% increase) and from 5 ±1 to 16 ±1 g_{CO2} m^{-3} h^{-1} (220% increase). The increase of P_{CO_2} against of the CH_4 RE decrease was in agreement with the ethanol complete removal in the bottom sections of both biofilters.

According to Figures 5.3a and b, the CH_4 REs of the middle sections for SBF and HBF varied in the range of 17 ±1 to 19 ±1% and 17 ±2 to 24 ±4 % respectively during Phases 1 to 5. The middle section CH_4 RE variations over Phases 1 to 5 is linked to P_{CO_2} variations from 4 ±0.5 to 6 ±1 g_{CO2} m^{-3} h^{-1} and from 6 ±1 to 8 ±0.5 g_{CO2} m^{-3} h^{-1} for SBF and HBF respectively (Figures 5.4a and b). Gómez-Cuervo et al. (2016) [34] reported a contribution of the biofilter lowest section as high as 19% compared to 2 and 13% for middle and top sections respectively of a CH_4 biofilter with a CH_4 IL of 16 g_{CH4} m^{-3} h^{-1}. Carbon dioxide production rates (P_{CO_2}s) of 12, 1 and 3 g_{CO2} m^{-3} h^{-1} were obtained respectively for the bottom, middle and top sections in accordance with their corresponding CH_4 REs [34] similarly to the present study.

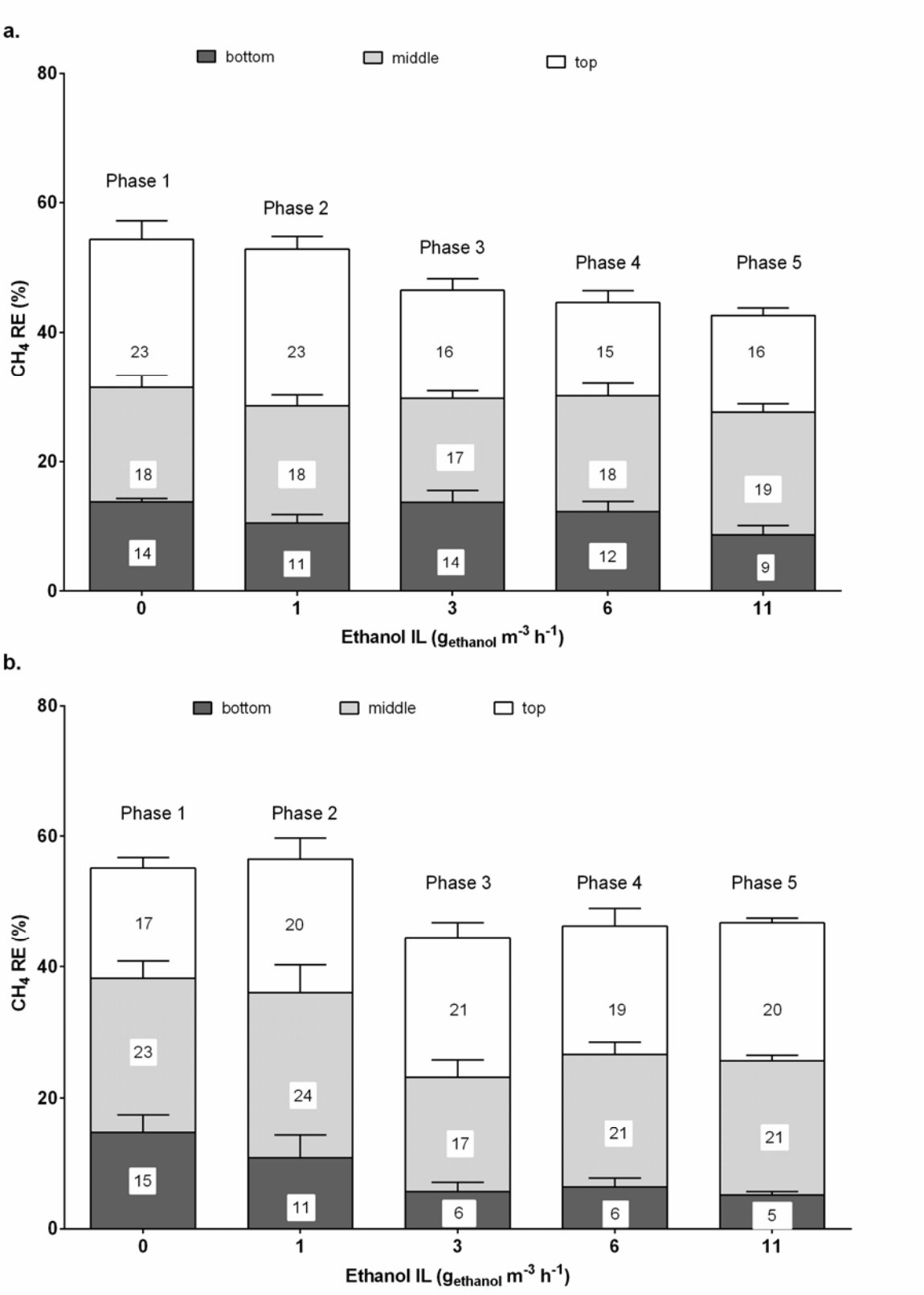

Figure 5.3: Methane (CH_4) removal profile across the filter bed as a function of ethanol IL a. SBF, b. SBF

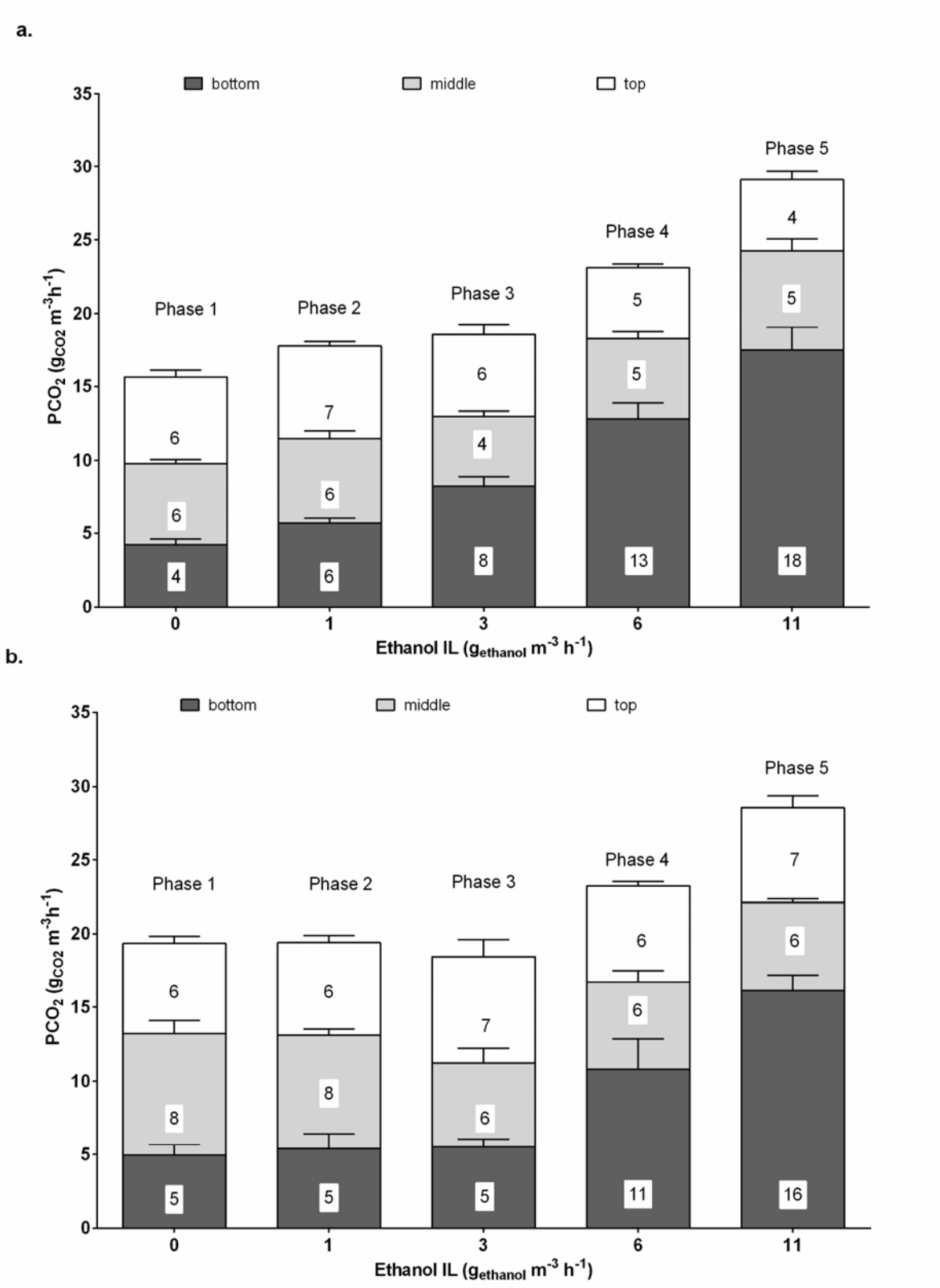

Figure 5.4: Carbon dioxide production rate (P CO_2) profile across the filter bed as a function of ethanol IL. a. SBF, b. HBF

According to Figures 5.3a and b, the top section CH_4 REs of the SBF decreased from 23 ±3 to 16 ±1%. This reduction was linked to the corresponding P_{CO_2} slight reduction from 7 ±0.5 to 4 ±0.5 g_{CO2} m^{-3} h^{-1} (Figures 4a and b). The CH_4 RE and P_{CO_2} for top section of the HBF slightly varied in the range of 17 ±1% to 21 ±1% with a corresponding P_{CO_2} of 6 ±1 g_{CO2} m^{-3} h^{-1} respectively. The variations of CH_4 REs in the middle and top sections of the biofilters over Phases 2 to 5 could be a result of excess biomass production or microbial population changes. In addition, a trace amount of ethanol vapors as well as trace toxic intermediates (e.g., acetaldehyde, acetic acid and ethyl acetate) [167] might reach the upper sections of the biofilters and caused a slight performance reduction.

5.5.3 Ethanol concentration in the leachate

Figures 5.5a and b show the ethanol concentration in the leachate for the SBF and HBF respectively over Phases 2 to 5 corresponding to ethanol IL variations in the gas phase from 1 ±0.5 to 11 ±0.5 $g_{ethanol}$ m^{-3} h^{-1} under a constant CH_4 IL of 13 ±0.5 g_{CH4} m^{-3} h^{-1}. For SBF, over Phases 2 and 3 (ethanol ILs ranging from 1 ±0.5 to 3 ±0.5 $g_{ethanol}$ m^{-3} h^{-1}), no ethanol was detected in the leachate. However, ethanol IL increase from 3 ±0.5 to 6 ±0.5 $g_{ethanol}$ m^{-3} h^{-1} (Phases 4) resulted in an average ethanol concentration in the leachate as 900 ±500 $g_{ethanol}$ $m^{-3}_{leachate}$. When the ethanol concentration approximately doubled in the gas Phase from 6 ±0.5 to 11 ±0.5 $g_{ethanol}$ m^{-3} h^{-1} (Phase 5), ethanol concentration in the leachate increased more than 2 fold from 900 ±500 g m^{-3} to 2200 ±400 $g_{ethanol}$ $m^{-3}_{leachate}$.

For HBF (Figure 5.5b), over Phases 2 and 3, an average ethanol concentration in the leachate lower than 150 $g_{ethanol}$ $m^{-3}_{leachate}$ was detected for corresponding ethanol ILs ranging from 1 ±0.5 to 3 ±0.5 $g_{ethanol}$ m^{-3} h^{-1}. Accordingly, when the ethanol IL was increased from 3 ±0.5 to 6 ±0.5 $g_{ethanol}$ m^{-3} h^{-1} (Phase 4), ethanol concentration in the leachate increased to 1600 ±900 $g_{ethanol}$ $m^{-3}_{leachate}$. Finally at Phase 5, increasing the ethanol IL from 6 ±0.5 to 11 ±0.5 $g_{ethanol}$ m^{-3} h^{-1}, resulted to an ethanol concentration in the leachate increase from 1600 ±900 $g_{ethanol}$ $m^{-3}_{leachate}$ to 2300 ±400 $g_{ethanol}$ $m^{-3}_{leachate}$. According to Figures 5.5a and b, the HBF flushed a slightly larger amount of ethanol (5% more) in the leachate compared to SBF over phases 2 to 5. The inorganic balls in the HBF might have less ability in terms of ethanol retention in the biofilm phase compared to the stones in the SBF.

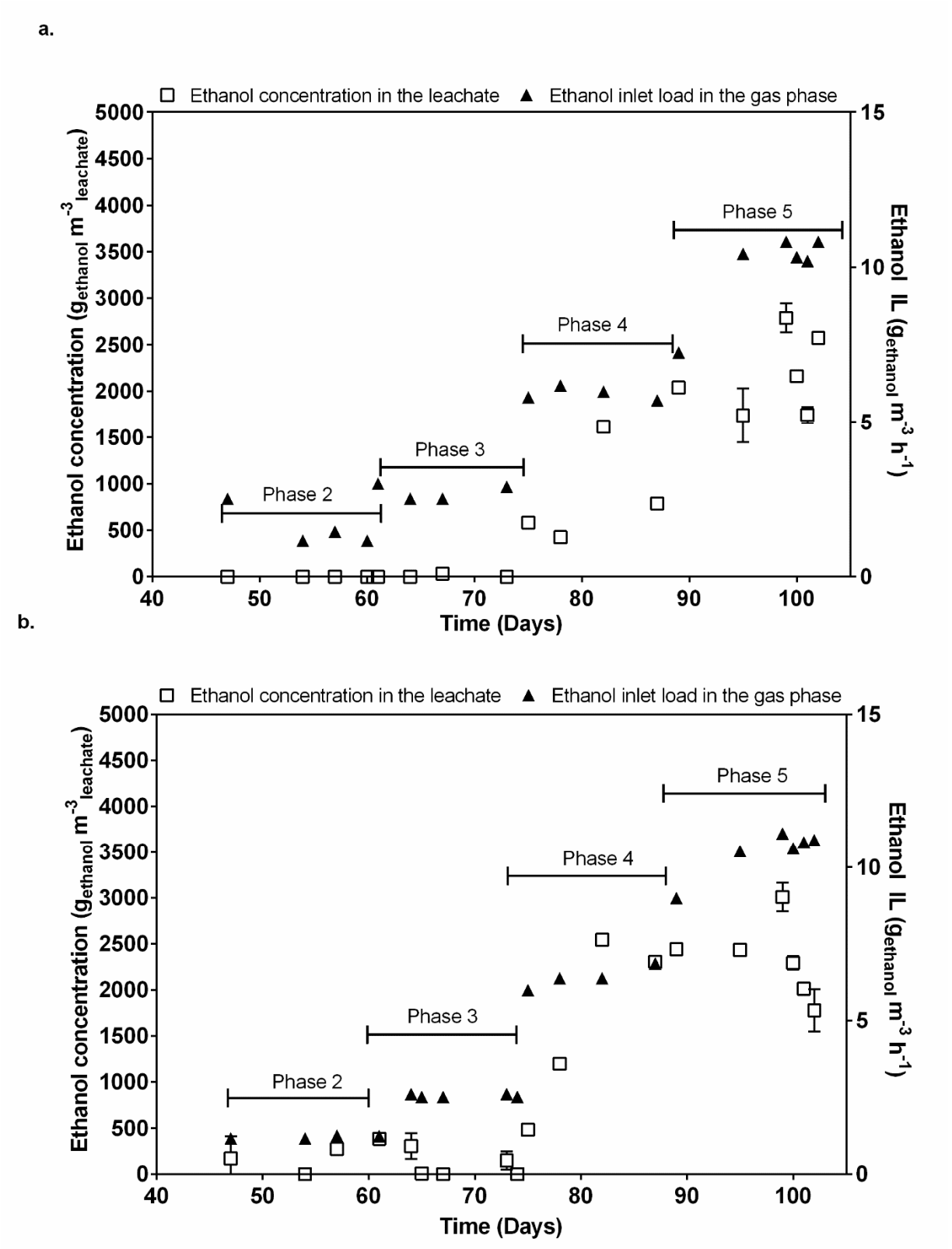

Figure 5.5: Ethanol concentration in the leachate as a function of time. a. SBF, b. HBF

Another possibility for low ethanol concentration in the leachate of SBF compared to HBF could be the higher rate of ethanol biodegradation into CO_2 in the SBF bottom section compared to HBF. For SBF, the bottom section P_{CO_2}s were in the range of 4 to 18 g_{CO2} m^{-3} h^{-1} whereas for HBF P_{CO_2}s were in the range of 6 to 16 g_{CO2} m^{-3} h^{-1} (Figures 4a and b).

The presence of ethanol in the leachate of the biofilters could be attributed to enhanced ethanol mass transfer from gas into the biofilm phase as well as the miscibility of ethanol with water [5]. A few studies analyzed the alcohol concentration in the leachate of biofilters. Morotti et al. (2011) [55] observed an increase, similar to the current study, for ethanol concentration in leachate of an inorganic-based bed biofilter increasing from 1000 to 12000 $g_{ethanol}$ $m^{-3}_{leachate}$ for a corresponding ethanol IL increasing from 25 to 125 $g_{ethanol}$ m^{-3} h^{-1}. A higher ethanol concentration in the leachate (1000 to 12000 $g_{ethanol}$ $m^{-3}_{leachate}$) was obtained compared to the current study possibly because of the lower ethanol ILs in the present study (1±0.5 to 11±0.5 g m^{-3} h^{-1}).

5.5.4 The performance of SBF and HBF under transient conditions

Figures 5.6 (a-c) and Figures 5.7 (a-c) show the SBF and HBF dynamic behavior respectively in terms of CH_4 RE, P_{CO_2} and the ethanol concentration in leachate. The transient conditions for both biofilters for an ethanol shock load at a constant CH_4 IL of 13 ±0.5 g_{CH4} m^{-3} h^{-1} (Phases a and b) were followed by a starvation (absence of nutrients, CH_4 and ethanol) (Phases c and d). A sudden variation of ethanol IL from 11 ±0.5 to 52 ±1 $g_{ethanol}$ m^{-3} h^{-1} (almost 5 fold increase) for 4 days (days 103 to 106) (Phase a) suddenly dropped CH_4 REs from 41% (day 102) to 31% (day 103) (25% decrease) for SBF (Figure 5.6a) and from 47% (day 102) to 34% (day 103) (28% decrease) for HBF (Figure 5.7a). However, the shock load had no influence on the ethanol RE (RE=100%) for both biofilters. During the ethanol shock load (days 103 to 106), CH_4 RE remained at 32 ±2% and 35 ±2% for the SBF and HBF respectively. After the shock load (Phase b), when the ethanol IL was restored to 11 $g_{ethanol}$ m^{-3} h^{-1}, the CH_4 REs for the SBF and HBF gradually improved to 37% and 44% respectively over 4 days (days 107 to 110). López et al. (2014) [63] observed that a shock load of a kinetic limited pollutant (methanol) from 50 to 600 g m^{-3} h^{-1} dropped the mass transfer limited pollutant (α-pinene) RE from 40 to 5% (α-pinene IL=25 g m^{-3} h^{-1}) in a biofilter while methanol RE of 90% remained unchanged.

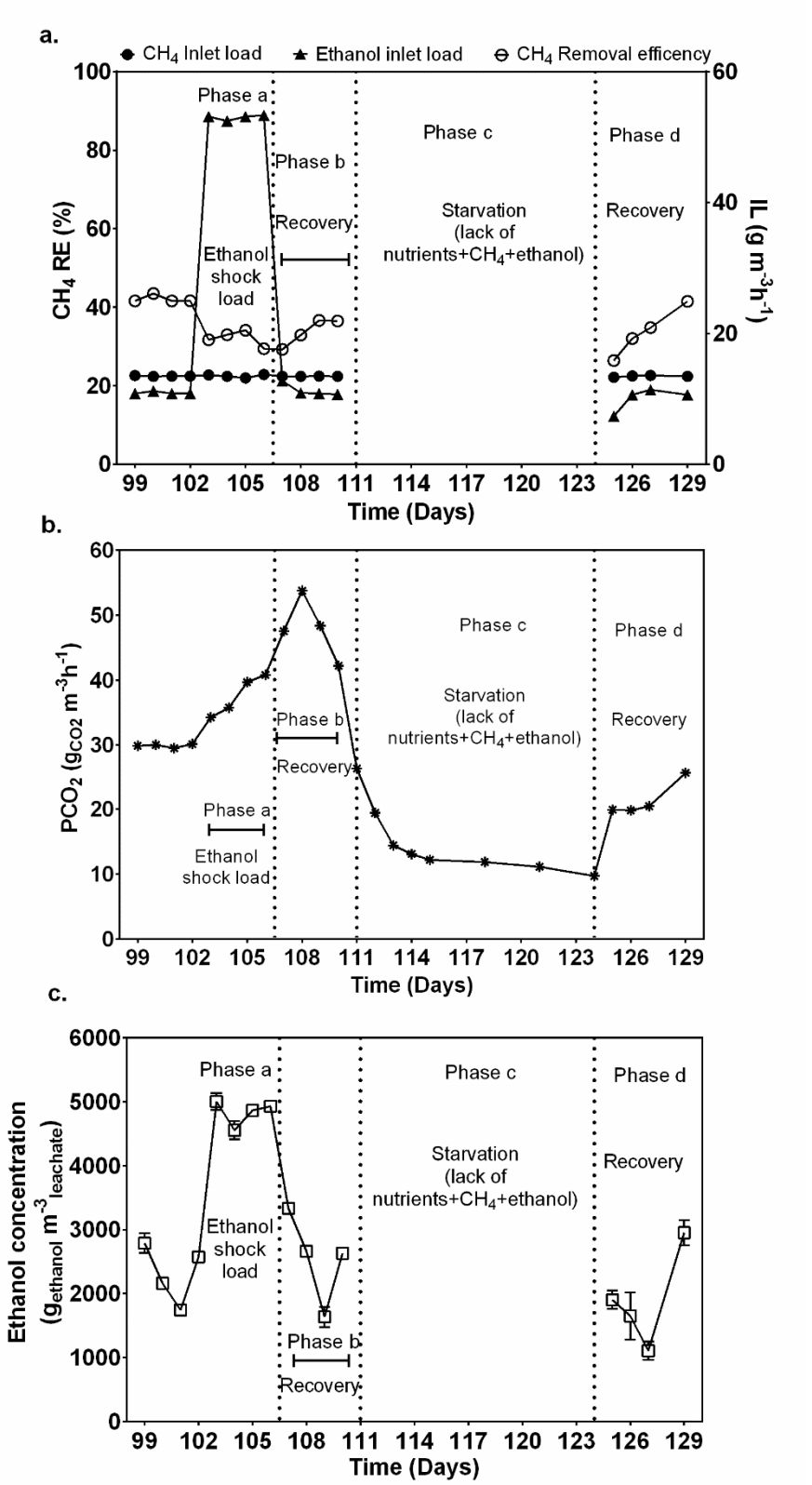

Figure 5.6: Transient conditions for the SBF as a function of time. a. CH_4 removal efficiency, b. CO_2 production, c. Ethanol concentration in the liquid effluent

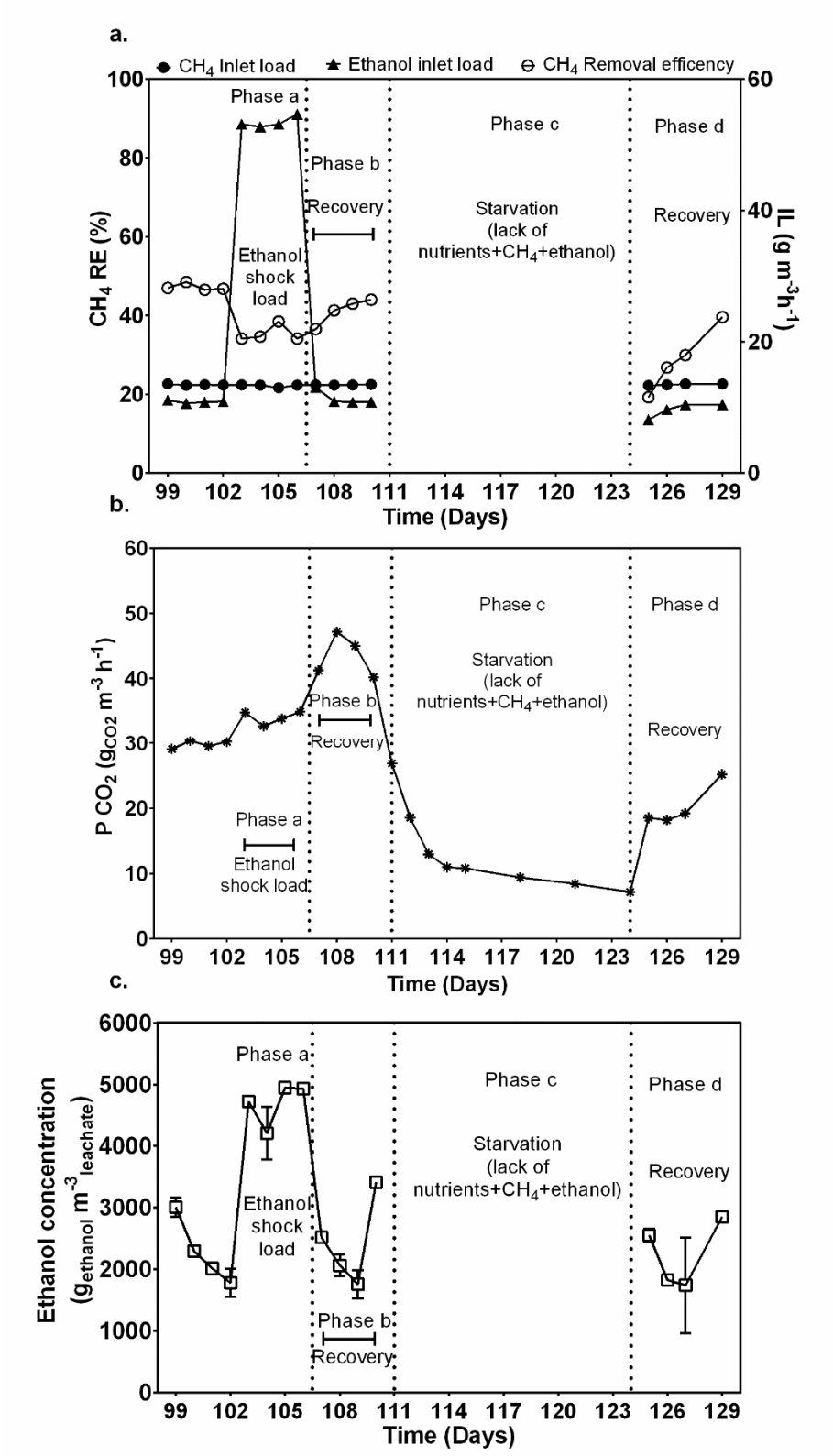

Figure 5.7: Transient conditions for the HBF as a function of time. a. CH_4 removal efficiency, b. CO_2 production, c. Ethanol concentration in the liquid effluent

According to Figures 5.6a and 5.7a, the following 14 days of starvation (days 111 to 124) (Phase c) diminished CH_4 REs from 37 to 27% (27% decrease) and from 44 to 19% (57% decrease) for the SBF and HBF respectively. However, over 5 days after the starvation (Phase d), the SBF and HBF were recovered partially in terms of CH_4 REs from 27 to 41% and from 19 to 40% respectively.

According to Figures 5.6b and 5.7b, P_{CO_2}s were gradually improved from 30 to 40 g_{CO2} m^{-3} h^{-1} (33% increase) and from 30 to 35 g_{CO2} m^{-3} h^{-1} (16% increase) for the SBF and HBF respectively when the ethanol shock load was applied (days 103 to 106) (Phase a). However, the improvement of P_{CO_2}s from 40 to 54 g_{CO2} m^{-3} h^{-1} (35% increase) and from 35 to 47 g_{CO2} m^{-3} h^{-1} (34% increase) for the SBF and HBF respectively occurred during the following 2 days (days 107 to 108) (Phase b) after the end of the ethanol shock load . The continuing P_{CO_2}s increase for 2 days after the end of shock load was probably due to the accumulation of ethanol in the biofilm phase. Subsequently, P_{CO_2}s dropped to 42 g_{CO2} m^{-3} h^{-1} and 40 g_{CO2} m^{-3} h^{-1} for the SBF and HBF respectively during the following 2 days (days 109 and 110). According to Figures 5.6b and 7b, during the starvation period, CO_2 was still produced with a decreasing trend from 26 to 10 g_{CO2} m^{-3} h^{-1} (61% decrease) and from 27 to 7 g_{CO2} m^{-3} h^{-1} (74% decrease) for the SBF and HBF respectively. The P_{CO_2} reduction for the HBF was more significant compared to SBF. This was in an agreement with the more significant CH_4 REs reduction for HBF (57% decrease) compared to SBF (27% decrease) before and after the starvation. Carbon dioxide production over the starvation period could be as a result of ethanol residuals biodegradation in the biofilm phase [168]. Another possibility might be an endogenous respiration or consumption of extracellular polymeric substrate (EPS) as an alternate substrate [168, 169]. One day after starvation (day 125), P_{CO_2}s immediately increased from 10 to 20 g_{CO2} m^{-3} h^{-1} (SBF) and from 7 to 18 g_{CO2} m^{-3} h^{-1} (HBF). The rapid improvement of P_{CO_2} after the starvation indicated the ability of the microbial culture of the biofilters to withstand lacks of nutrients and substrates for 2 weeks. The P_{CO_2}s increased to 25 g_{CO2} m^{-3} h^{-1} in the following 5 days (days 125 to 129) for both biofilters.

According to Figures 5.6c and 5.7c, the ethanol shock load of 5 fold its original value, resulted in a sudden 2 fold increase of ethanol concentration in the leachate from 2600 to 5000 $g_{ethanol}$ $m^{-3}{}_{leachate}$ for SBF and from 2600 to 4700 $g_{ethanol}$ $m^{-3}{}_{leachate}$ for HBF. Nevertheless, according to

Figures 5.6b and 5.7b, the P_{CO_2}s improvement was slow during the shock load. The exceeding ethanol absorption in the biofilm phase compared to ethanol biodegradation rate during the shock load may have resulted in an immediate accumulation of ethanol in the biofilm phase for both biofilters and consequently in their leachates. After ethanol IL restoration, the ethanol concentration in the leachate for SBF decreased from 5000 to 2600 $g_{ethanol}$ $m^{-3}_{leachate}$ in 2 days (days 107 and 108). Nevertheless, when the shock load ended, the ethanol concentration in the HBF leachate immediately dropped back to its original value of 2500 $g_{ethanol}$ $m^{-3}_{leachate}$. The immediate restoration of HBF compared to SBF in terms of ethanol concentration in its leachate was likely related to the packing materials. The HBF inorganic balls might have less potential to retain ethanol compared to the SBF stones.

The responses of both biofilters after the ethanol shock load or starvation were quick. Both biofilters were recovered up to 90% of their original performances during 4 and 5 days after the shock load and the starvation respectively.

5.5.5 Pressure drop evolution

Figure 5.8 shows the global and the bottom section pressure drops for SBF over 129 days of operation under steady and transient state conditions. It should be noted that the global and bottom section pressure drops corresponded to 1 m and 0.33 m of the biofilters bed height (H) respectively. Under steady state conditions, over Phases 1 to 5 (days 1 to 102), the global pressure drop slightly increased from 0.05 to 0.30 cmH_2O for a constant CH_4 IL of 13 ±0.5 $g_{ethanol}$ m^{-3} h^{-1} and an ethanol IL variation from 1 ±0.5 to 11 ±0.5 $g_{ethanol}$ m^{-3} h^{-1}. The bottom section pressure drop also increased from 0.02 to 0.25 cmH_2O. The contribution of the bottom section in the global pressure drop was more than 80%; possibly due to biomass production in the bottom section as a result of ethanol biodegradation. When the ethanol shock load from 11 to 52 $g_{ethanol}$ m^{-3} h^{-1} was applied, the global and the bottom section pressure drops temporarily increased 2 fold from 0.30 to 0.65 cmH_2O (days 102 to 104) and from 0.25 to 0.60 cmH_2O respectively, then declined to their original values of 0.30 cmH_2O and 0.23 cmH_2O. When the ethanol IL restored to its original value of 11 $g_{ethanol}$ m^{-3} h^{-1} (days 107 to 110), the global and bottom section pressure drops increased again from 0.30 to 0.45 cmH_2O and from 0.25 to 0.40 cmH_2O respectively.

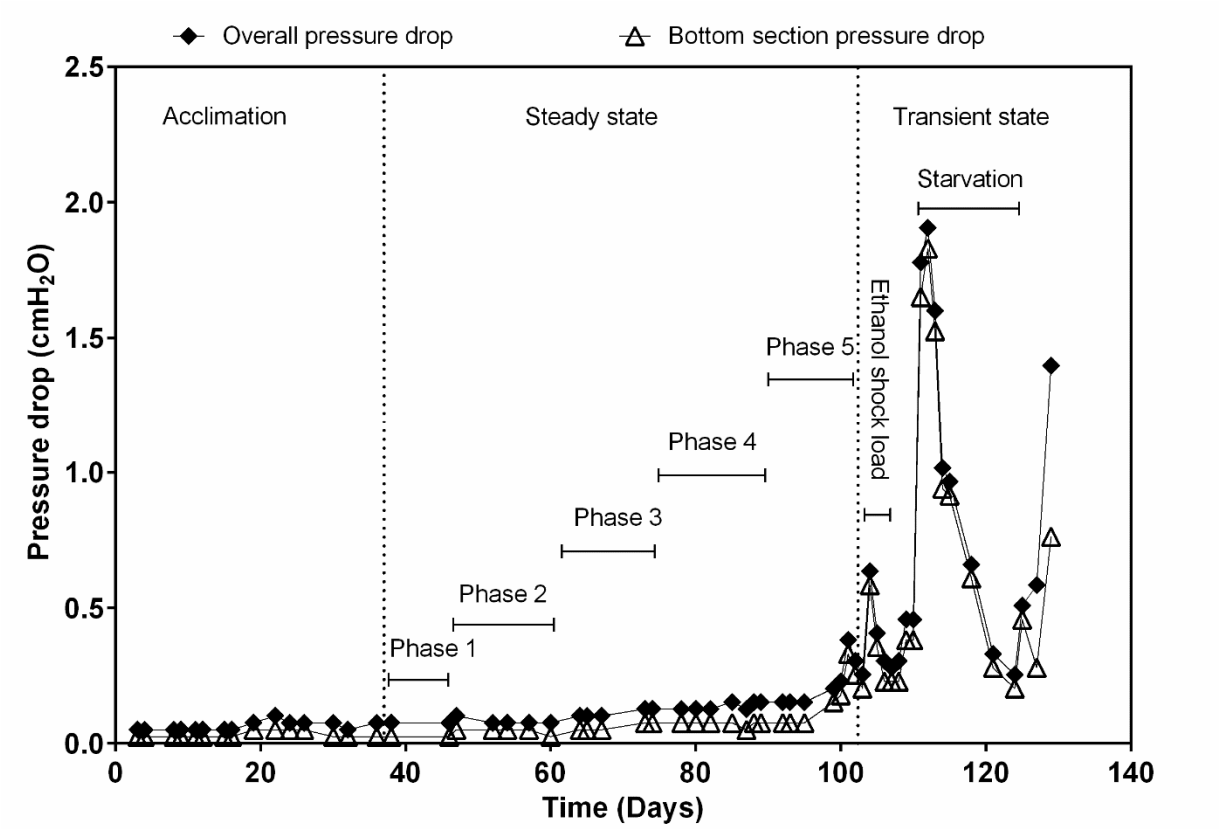

Figure 5.8: Overall pressure drop (filter bed height (H) =1 m) and bottom section pressure drop (H=0.33 m) for SBF as a function of time

The higher pressure drop during the shock load (days 103 to 106) and recovery (days 107 to 110) periods could be attributed to excess biomass growth as a result of excess ethanol in the biofilm phase. The excess biomass growth was also observed visually at the bottom section compared to middle and top sections of SBF. Ryu et al. (2010) [83] reported an increasing pressure drop from 1 to 10 cmH_2O m^{-1} as a result of biomass accumulation increase from 0.8 to 3 $g_{biomass}$ $g_{packing}^{-1}$ in a polyurethane foam bed biofilter for benzene removal with corresponding IL of 600 g m^{-3} h^{-1}. When the starvation was started for the SBF, the global and bottom section pressure drops rose dramatically from 0.45 to 1.90 cmH_2O and from 0.40 to 1.85 cmH_2O during the first 2 days (days 110 to 112) possibly according to the lack of irrigation by the daily nutrient solution addition (1 L min^{-1} day^{-1}). Biofilter daily irrigation is an efficient technique which detaches a fraction of the biomass from the packing materials and prevents an excess biomass accumulation [163]. The dissolved biomass was observed visually in the leachate of SBF. However, during the rest of the starvation period, the global and bottom section pressure drops

decreased from 1.90 to 0.25 cmH_2O and from 1.80 to 0.20 cmH_2O respectively. The excess biomass growth during the starvation period was limited by reducing the biofilm activity under the lack of carbon sources (CH_4+ethanol) as well as essential nutrients (e.g., nitrogen, phosphorous) [82]. When the starvation was finished, the global and the bottom section pressure drops increased again from 0.25 to 1.40 cmH_2O and from 0.20 to 0.75 cmH_2O respectively for a corresponding CH_4 IL of 13 g_{CH4} m^{-3} h^{-1} and an ethanol IL of 11 $g_{ethanol}$ m^{-3} h^{-1}.

For HBF, the pressure drop variation was negligible for both steady state and transient state conditions. The global and bottom section pressure drops for HBF remained constant as 0.05 cmH_2O and 0.02 cmH_2O during 129 days of operation. The excess pressure drop of the SBF compared to the HBF could be as a result of different packing materials of the bottom sections. The small diameter of the stone ($(7\pm1)*10^{-3}$ m) compared to the inorganic ball ($(12\pm4)*10^{-3}$ m) increased the pressure drop [15]. Fewer empty spots among stones were available compared to the inorganic balls for excess biomass occupation.

5.6 Conclusion

Two inorganic bed biofilters with different packing materials in their bottom sections as stones (SBF) or inorganic balls (HBF) were employed to eliminate CH_4 in the absence and presence of ethanol. For CH_4 individual removal, both biofilters reached a total CH_4 RE of 55 ±1% for a corresponding CH_4 IL of 13 ±0.5 $g_{ethanol}$ m^{-3} h^{-1}. The presence of ethanol from 1 to 11 ±0.5 $g_{ethanol}$ m^{-3} h^{-1} diminished the CH_4 REs from 55 ±1% to 43% ±1% and from 55 ±1% to 46 ±1% for SBF and HBF respectively due to ethanol toxic effect on methanotrophs.

Around 1/4 of the CH_4 elimination happened in the biofilter bottom sections. Nevertheless, the packing materials in the bottom sections played an important role when ethanol was fed to the CH_4 biofilters. Ethanol was entirely removed in the bottom section while CH_4 REs were decreasing. Ethanol complete elimination was a result of mineralization to CO_2 as well as dissolving in the leachate of the biofilter while nutrient solution was supplied.

For transient state conditions, both biofilters tolerated 4 days ethanol shock (11 to 53 $g_{ethanol}$ m^{-3} h^{-1}) followed by 14 days of nutrient and substrate starvations. The shock load had no effect on ethanol complete removal. However, a 20% decrease of CH_4 RE followed by the alcohol shock load or the starvation occurred for both biofilters. Subsequently, during a period of 4 and 5 days after the shock load and the starvation respectively, both biofilters recovered up to 90%

of their original performance. The stones as a filter bed were more likely to produce excess pressure drop comparing with inorganic balls. The SBF pressure drop rose over the time up to 1.9 $cmH_2O\ m^{-1}$. However, the HBF pressure drop remained unchanged at 0.05 $cmH_2O\ m^{-1}$. Around 80% of the stone-based bed biofilter pressure drop was generated in its bottom section where ethanol biodegradation produced excess biomass. Starvation was an efficient strategy to reduce the pressure drop.

5.7 Acknowledgments

M. Heitz and J.P. Jones would like to acknowledge the Natural Science and Engineering Research Council of Canada (NSERC) which financially supported this research.

CHAPTER 6. Conclusion

Biofilters have been applied for the elimination of organic pollutants (e.g., methane (CH_4), benzene, toluene, etc.) via bioxidation. Two important sorts of mass transfer or kinetic limitations can occur in a typical organic pollutant's removal in a biofilter. In this regard, two groups of mass transfer limited and kinetic limited organic pollutants were defined. Water solubility, dimensionless Henry's law constant and vapor pressure of pollutants were three physico-chemical properties which were discussed in order to consider a pollutant as a mass transfer or kinetic limited pollutant. Organic pollutants with low water solubility (<500 g m^{-3}), high dimensionless Henry's law constant (>0.1) and high vapor pressure (>5000 kPa) were named as mass transfer limited pollutants. On the other hand, miscible organic pollutants with water with low dimensionless Henry's law constant (<0.1) and low vapor pressure (<30 kPa) were named as kinetic limited pollutants. Methane and ethanol are examples of mass transfer limited pollutant and kinetic limited pollutant respectively. The appropriate operating parameters like packing materials or empty bed residence time (EBRT) are different for the elimination of mass transfer or kinetic limited pollutants in biofilters. Thus, when mass transfer and kinetic limited pollutants are present in a mixture, the operating parameters (e.g., packing materials, EBRT) should be suitable for both types of pollutants in order to minimize the limitations.

Methane elimination in the presence of ethanol vapors under steady and transient state conditions was the main objective of this study. Methane (CH_4) is a mass transfer limited pollutant with hazardous impacts for global warming. Ethanol is a kinetic limited pollutant which is often present in a mixture with CH_4 emissions particularly at ethanol industries. Biofilter operation under transient conditions (e.g., shock load, intermittent load, and starvation) is an important requirement for industrial applications. In addition, transient conditions make a better understanding about the phenomena and limitations in biofiltration.

The first specific objective of this study was to evaluate CH_4 removal in a stone-bed biofilter under steady and transient state conditions. Under steady state condition, the effect of CH_4 inlet concentration ranging from 1000 to 13000 ppmv on the biofilter performance at a fixed EBRT of 6 min were studied. In general, increasing the CH_4 inlet concentration gradually dropped the

CH_4 removal efficiency (RE) from 87 to 52%. However, the CH_4 RE reduction from 75 to 52% was more significant when the CH_4 inlet concentration exceeded 4000 ppmv. Therefore, the critical CH_4 inlet concentration was 4000 ppmv. A maximum elimination capacity (EC_{max}) of 45 g m^{-3} h^{-1} was obtained for the highest CH_4 inlet load (IL) of 87 g m^{-3} h^{-1} with corresponding RE of 52%. Transient conditions were applied to the biofilter by two types of shock loads and three strategies of starvation. The CH_4 shock loads from 13 to 65 g m^{-3} h^{-1} either by changing CH_4 inlet concentration from 2000 to 10000 ppmv or by changing gas flow rate from 3 to 15 L min^{-1}, were tolerable for the CH_4 biofilter. The biofilter recovery after the shock loads were instantaneous. Three strategies for starvation were conducted by nutrient starvation (14 days), addition of tap water instead of nutrient solution (14 days) and a lack of CH_4 and nutrients (1 month) at Steps 1, 2 and 3 respectively. The lack of nutrients and tap water addition (Steps 1, 2) had no significant impact on the biofilter performance. However, the simultaneous lack of nutrients and CH_4 (Step 3) significantly dropped the CH_4 RE from 70 to 10%. A 5-day recovery time was needed for the biofilter after nutrient and CH_4 starvation (Step 3). In general, the biofilter displayed a promising performance under transient conditions in terms of flexibility, maintaining the microbial activity and quick recovery.

The second specific objective of this study was to evaluate the steady state performance and dynamic behavior of a CH_4 biofilter under three cycles of ethanol addition. Cycles 1, 2 and 3 corresponded to EBRTs of 6, 3 and 1.5 min respectively. At each EBRT, the biofilter performance for CH_4 removal was studied before and after the ethanol addition cycle in order to evaluate the transient conditions of the biofilter. Methane and ethanol ILs varied in ranges of 33 to 132 g_{CH4} m^{-3} h^{-1} and from 4.5 to 18 $g_{ethanol}$ m^{-3} h^{-1} respectively corresponding to an EBRT reduction from 6 to 1.5 min. The EBRT reduction dropped the CH_4 RE from 35 to 7% with no influence on ethanol RE of 100%. In addition, the presence of ethanol over the 3 cycles, also reduced the CH_4 RE from 35 to 0% probably due to toxic effects of the alcohol for methanotrophs. The most significant CH_4 RE decline from 7 to 0% in the presence of ethanol occurred at Cycle 3 for corresponding CH_4 IL of 132 g_{CH4} m^{-3} h^{-1} and ethanol IL of 18 $g_{ethanol}$ m^{-3} h^{-1} at an EBRT of 1.5 min. When both CH_4 and ethanol vapors were present, the maximum EBRT of 6 min, corresponding to CH_4 IL of 33 g_{CH4} m^{-3} h^{-1} and ethanol IL of 4.5 $g_{ethanol}$ m^{-3} h^{-1}, was an appropriate operating condition for CH_4 and ethanol removal in a mixture. In addition, the dynamic behavior of the biofilter in terms of CH_4 REs was studied after each cycle

in order to evaluate the biofilter resumption. The biofilter recovery after Cycles 1, 2 and 3 took 10, 14 and 25 days. The shortest EBRT of 1.5 min at Cycle 3 corresponding to the highest ethanol IL of 18 $g_{ethanol}$ m^{-3} h^{-1} ended up to the longest recovery time of 25 days for the CH_4 biofilter. The biofilter recovery time was linked to the ethanol concentration in the liquid effluent (leachate). The ethanol concentration in the leachate over Cycle 3 was obtained as 2500 $m^{-3}_{leachate}$ which was two-fold exceeding Cycles 1 and 2.

The third specific objective of this study was to compare a stone-bed biofilter (SBF) with a hybrid packing biofilter (HBF) for elimination of CH_4 and ethanol in a mixture under steady and transient state conditions. The SBF and HBF were different in terms of packing materials for their bottom section. Both biofilters reached a CH_4 RE of 55% for a CH_4 IL of 13 g m^{-3} h^{-1} in the absence of ethanol under steady state condition. The bottom sections in the biofilters had a key role when both pollutants were present. Ethanol was entirely removed in bottom sections of both biofilters for corresponding ethanol IL variation from 1 to 11 g m^{-3} and an EBRT of 6 min. The presence of ethanol vapors (ILs from 1 to 11 g m^{-3}) declined the CH_4 REs from 14 to 9% and from 15 to 5% in the bottom sections of the SBF and HBF respectively. In general, the SBF presented relatively a more promising performance in the presence of ethanol compared to the HBF. Transient conditions were applied by a 4 days of ethanol shock (11 to 52 g m^{-3} h^{-1}) followed by a 14 days of nutrient and substrate starvation. Both biofilters tolerated the transient condition with no interruption for complete ethanol removal and only 20% decrease of CH_4 RE. Both biofilters recovered promptly in periods of 4 and 5 days after the shock load and the starvation respectively. Excess pressure drop for SBF up to 1.9 cmH_2O m^{-1} was an important concern compared to HBF. The bottom section of SBF, where ethanol conversion occurred, contributed to 80% of the total pressure drop. The different bottom section packing material at HBF reduced the excess pressure drop. At HBF, the pressure drop remained at 0.05 cmH_2O m^{-1}. In addition, the 14-day starvation period, was a promising strategy for pressure drop reduction from 1.9 to 0.25 cmH_2O m^{-1}.

In general, this study displayed a promising potential of CH_4 biofilters to encounter with different transient conditions in terms of shock loads, starvations and periodic presence of alcohols. Although transient conditions usually provided harsh and unfavorable situations, the microbial culture especially methanotrophs were able to maintain their activity with a quick recovery and re-acclimation. In addition, this study showed the importance of some operating

parameters such as EBRT and packing materials for mass transfer and kinetic limited pollutants elimination in a mixture in biofilters. The hybrid bed biofilter (HBF) with a corresponding EBRT of 6 min showed the least limitations in terms of mass transfer and kinetic limitations for CH_4 and ethanol elimination in a mixture.

6.1 Conclusion in French

L'objectif principal de cette étude visait l'élimination du méthane (CH_4) en présence de vapeurs d'éthanol en régimes permanent et transitoire par biofiltration. Le CH_4 est un composé à limitation par transfert de masse et un des gaz à effet de serre à l'origine du réchauffement climatique. L'éthanol est un composé organique à limitation cinétique pouvant se trouver dans un mélange gazeux en présence de CH_4 telles les émissions issues de traitement des eaux.

En absence d'éthanol, en augmentant la concentration à l'entrée du CH_4 de 100 à 1300 ppmv (charge à l'entrée variant entre 8 et 87 g m^{-3} h^{-1}), la conversion (RE) a diminué de 87 à 52 %. Une capacité d'élimination maximale (EC_{max}) de 45 g m^{-3} h^{-1} a été obtenue pour une charge de CH_4 à l'entrée maximale de 87 g m^{-3} h^{-1} correspondant à une RE de 52 %.

En général, la présence d'éthanol diminue la capacité d'élimination du CH_4, étant donné la toxicité de l'éthanol pour les méthanotrophes. Par exemple, la conversion du CH_4 a diminué de 7 à 0 % en présence d'éthanol pour des charges de CH_4 de 132 g m^{-3} h^{-1} et des charges d'éthanol de 18 g m^{-3} h^{-1} sous un temps de résidence en fût vide de 1.5 min. Cependant la conversion de l'éthanol était totale. Ce dernier résultat peut être expliqué par l'accumulation d'éthanol dans le biofilm ou par la biodégradation de ce composé. Par contre, la solubilité de l'éthanol dans le biofilm produit davantage de biomasse et induit une perte de charge dans le biofiltre de 1.9 cm H_2O m^{-1}.

En général, cette étude prouve le potentiel des biofiltres pour le traitement du CH_4 que ce soit en régime transitoire ou en période de carence. Quoique le régime transitoire crée un environnement non favorable et contraignant vis-à-vis de la flore microbienne à savoir les méthanotrophes, ces dernières ont pu maintenir leurs activités après une carence en polluants et nutriments. Toutefois, cette carence permet de diminuer la perte de charge dans le biofiltre.

De plus, cette étude a montré l'importance de plusieurs paramètres opératoires tels l'EBRT et le garnissage pour l'élimination de composés à limitations liées au transfert de masse ou à la

cinétique dans un mélange. Un biofiltre mixte ayant 2 lits filtrants opérant sous un temps de résidence de 6 minutes a démontré peu de contraintes vis-à-vis de 2 polluants (CH_4 et éthanol) à limitations respectives par transfert de masse et cinétique présents dans un mélange.

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